### RESEARCH



# Theoretical study on the alkyl chain length impact of azobenzene-based photoresponsive ionic liquids

Liyao Ying<sup>1</sup>, Zhaoyang Ju<sup>1\*</sup>, Chunjin Lin<sup>2</sup>, Pin Wang<sup>2</sup>, Haixiang Cheng<sup>1</sup>, Liyong Ding<sup>1</sup>, Tianshu Chu<sup>3</sup>, Chunxiao Gong<sup>4</sup>, Bing Zhou<sup>5</sup>, Mengting Yu<sup>1\*</sup> and Chengsheng Ge<sup>1</sup>

### Abstract

The light-modulated isomerization and aggregation behavior of ionic liquids (ILs) in aqueous solutions holds fundamental and technological significance. Although several azobenzene-based photoresponsive ILs have been synthesized, there is still a lack of understanding regarding the aggregation mechanism, regularity of the alkyl chain length, and the position of the azobenzene (cis- and trans-) in these photoresponsive ILs. To elucidate the structureproperty relationship of photoresponsive ILs, four types of azobenzene groups photosensitive ILs ([AzoC, DMEA]Br, n = 2.4,6,10 in both trans- and cis- configurations were investigated by density functional theory (DFT) calculations. We investigated the geometric properties of cations, H-bonds interactions of ionic pairs, microstructures of clusters, and the interactions between ILs and water molecules. It was found that the molecular volume of cis- is smaller than that of trans- cation structures. Despite multiple H-bonds between the anions and the ammonium group of cations, longer alkyl chains weaken anion-cation interactions. The interaction energies of trans- n[AzoC\_DMEA] Br  $(1 \le n \le 4)$  clusters are stronger than those of *cis*-. Moreover, the interaction energy between *trans*-structures of photoresponsive ILs and water molecules is smaller than that of *cis*- structures based on the DFT calculations. The interaction energies per water molecule in the ILs-water clusters tend to saturation as the number of water molecules increases. The electrostatic interaction plays a crucial role in the stabilization of ILs and water systems. The structure-property relationship of photoresponsive ILs including the regularity of the alkyl chain length and the azobenzene position as well as the microscopic interaction mechanism of ILs and ILs-water clusters had been studied from theoretical calculation perspective. This work can contribute to an in-depth understanding of the microcosmic interactions of azobenzene-based photoresponsive ILs and aid in designing them in a "task-specific" way.

Keywords Ionic liquids, DFT calculations, Aggregation, Interactions, Clusters

\*Correspondence: Zhaoyang Ju jzy@qzc.edu.cn Mengting Yu 39090@qzc.edu.cn <sup>1</sup>College of Chemical and Material Engineering, Quzhou University, Quzhou, Zhejiang Province 324000, China <sup>2</sup>Zhejiang Geological Institute of Metallurgical Geology of China, Quzhou, Zhejiang Province 324000, China
<sup>3</sup>College of Resources and Environmental Sciences, China Agricultural University, Beijing 100193, China
<sup>4</sup>College of Engineering, Nanjing Agricultural University, Nanjing, Jiangsu Province 210031, China
<sup>5</sup>Zhejiang Jusheng Fluorination Chemical Co., Ltd., Quzhou, Zhejiang Province 324000, China



© The Author(s) 2025. **Open Access** This article is licensed under a Creative Commons Attribution-NonCommercial-NoDerivatives 4.0 International License, which permits any non-commercial use, sharing, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if you modified the licensed material. You do not have permission under this licence to share adapted material derived from this article or parts of it. The images or other third party material in this article are included in the article's Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit http://creative.commons.org/licenses/by-nc-nd/4.0/.

### Introduction

Stimulus-responsive materials, commonly termed smart materials, exhibit the capacity to detect external stimuli and reversibly return to their original state upon stimulus removal [1]. These materials find broad applications in advanced fields including biomedicine [2], sensors [3], and electrochemistry [4]. Unlike conventional stimuli, such as electrical, thermal, or magnetic inputs, light irradiation offers distinct advantages as an energy source due to its signal stability and spatial precision, making it particularly effective for regulating the dynamic responses of smart materials [5–7].

Ionic liquids (ILs), recognized as environmentally benign alternatives, have gained extensive application in organic synthesis, biocatalysis, separation processes, and preparation of functional materials due to their unique physicochemical properties [8–12]. Compared with traditional organic solvents, ILs demonstrate superior characteristics including negligible volatility, exceptional thermal stability, and wide electrochemical windows. ILs can be regarded as adjustable and designable solvents by adjusting the combination of anions and cations or by changing functional groups [13]. Their structural tunability through anion-cation combinations or functional group modifications enables rational design of photosensitive ILs. The photoresponsive ILs can transform into another state under the illumination of a certain wavelength and can return to their initial state under the illumination of another wavelength or other conditions. For example, azobenzene (AZB) can undergo reversible photo-induced *cis*- to *trans*- isomerization [14–16]. Diphenylethylene (DAEs) is prone to transitioning between two steady states under light conditions [17-20]; Spiropyrans (SPs) undergo a structural transition between closed-loop and open-loop configurations under light stimulation [21-23]. Photoinduced isomerization of the molecules could trigger the rearrangement of the building blocks to generate morphological or size transitions, which are essential for the functionality of photoresponsive materials.

As a widely employed photosensitive moiety, AZB serves as an exceptional molecular switch due to its environmental responsiveness, synthetic accessibility, and excellent cycling stability [24]. Yuan et al. [8] have synthesized 10 kinds of azobenzene-based ILs, and applied them as photosensitive surfactants to form micro lotion with water and various alcohols. Li et al. [25] studied the reversible phase transfer of six azobenzene-based ILs surfactants between organic and aqueous phases and explored in detail the factors affecting transfer. Notably, Ma et al. [26] found that under the bistable temperature, the photoinduced phase separation is completely reversible, and the photoinduced expansion and contraction are also reversible. Azobenzene-based ILs gel can be used

to realize an optical actuator at a suitable temperature. Most of the studies about photosensitive ILs are focused on the synthesis of photosensitive ILs, reversible reactions of photoisomerization, and phase transfer catalysis, but there is still a lack of fundamental research at the molecular level.

Recent advances in computational science have enabled researchers to investigate the microscopic characteristics of ionic liquids (ILs) through sophisticated modeling techniques, including molecular dynamic simulations (MD), ab initio, and density functional theory (DFT) to study the microcosmic characteristics of ILs [27-29]. Many researchers have reported the inner mechanisms of ILs in terms of gas absorption mechanisms, lignocellulose dissolution, and biomass-to-biofuel conversion by using DFT method [30-32]. Zheng et al. [33]explored the effects of different anionic alkyl chain lengths on the structure and interaction of choline-based ILs and found that the aggregation of anions in ILs was attributed to side chain interactions of anions. Hu et al. [34] used the DFT calculations to study the effects of different alkyl chain lengths of imidazole cations on the stability of surface active ILs hydrates and found that increasing alkyl chains is beneficial for improving stability. The aggregation behavior of ILs composed of 1-alkyl-3-methylimidazolium cations,  $[C_n mim]^+$  (*n* = 8, 10, 12) and trans-cinnamic acid anion can be efficiently modulated by UV light in aqueous solution [35]. However, there is currently no research exploring the effects of different alkyl chain lengths and aggregation mechanisms of photosensitive ILs using DFT methods. To gain a deeper insight into the correlation between azobenzene position and the photoresponsive properties/aggregation behavior of azobenzene-based ionic liquids, it is essential to investigate this class of ionic liquids where the azobenzene group is located in different positions within the alkyl chain.

As a typical case of photosensitive ILs which had successfully synthesized before by experibeen ment [36], four types azobenzene groups photosensitive ILs ([AzoC<sub>n</sub>DMEA]Br, n = 2,4,6,10) were calculated to investigate the influence of alkyl chain length on the trend of microscopic interactions, including 2-hydroxyethyl-dimethyl-[2-(4-phenylazophenoxy)-ethyl]-ammonium bromide [AzoC<sub>2</sub>DMEA] Br, 2-hydroxyethyl-dimethyl-[4-(4-phenylazo-phenoxy)- $[AzoC_4DMEA]Br$ , butyl]-ammonium bromide 2-hydroxyethyl-dimethyl-[6-(4-phenylazo-phenoxy)ethyl]-ammonium bromide [AzoC<sub>6</sub>DMEA]Br and 2-hydroxyethyl-dimethyl-[10-(4-phenylazo-phenoxy)ethyl]-ammonium bromide [AzoC<sub>10</sub>DMEA]Br (see Fig. 1) by using DFT calculations. To study the H-bonds interactions of trans- and cis- azobenzene-based ILs ([AzoC<sub>n</sub>DMEA]Br, n = 2,4,6,10), we investigated the



**Fig. 1** Chemical structure of azobenzene-based ionic liquids. ( $[AzoC_{n+1}DMEA]Br, n = 1,3,5,9$ )

effects of trans- and cis- on the structural properties. The geometries of cations, ionic pairs, clusters of azobenzene-based ILs, and ILs/water systems have been studied. The roles of water have also been considered in photoisomerization and aggregation behavior modulation. The microcosmic interaction energies and H-bonds of azobenzene-based ILs have been further analyzed by some theoretical methods such as atoms in molecules (AIM) theory, independent gradient model based on Hirshfeld partition (IGMH), and symmetry-adapted perturbation theory (SAPT). These analytical methods have been determined to provide useful information for the understanding of the structure-property relationship and the microscopic interaction of ILs. This fundamental study not only enhances our understanding of the microscopic H-bonding interactions in azobenzene-based photoresponsive ILs at the molecular level but also provides useful insights for the design of microscale photo-control devices and sensors.

### **Computational methods** Structures optimization

The optimization for all the structures of ILs was performed using Gaussian 16 program [37] and the figures were generated by using the Visual Molecular Dynamics (VMD) software [38]. Considering the dispersion interactions in the ILs system and enhancing its capability for noncovalent interactions, the method of dispersion correction (DFT-D) [39, 40] has been also considered in the structure optimization due to the higher accuracy and less empiricism. The hybrid Becke 3-Lee-Yang-Parr (B3LYP) exchange-correlation functional combined with D3 dispersion correction and with the  $6-31+G^{**}$ basis set was employed for the structure optimization and frequency calculations. The same method (B3LYP- $D3/6-31+G^{**}$ ) has been also studied and shown a good description of the interactions of ILs in the other DFT calculations [41, 42]. To find the most stable structure of the ionic clusters, 200 random initial configurations were generated using the Molclus program [43] (version 1.9.9.9) and optimized by a semi-empirical method at the PM7 level. Soyemi et al. [44] reported that the semiempirical methods including B97-3c and PBEh-3c perform better against coupled-cluster for calculating the dipole moment of organic molecules than that of PM6, and PM7. Besides, PM6 and PM7 would change the geometry and electron density distribution relative to the high-level DFT and overpredicted the dipole moment of molecules, but the computational cost of PM6, and PM7 are shorter than that of B97-3c and PBEh-3c. Besides, some studies have reported the semiempirical method PM7 combined with dispersion has shown a good description of the non-covalent interactions for macromolecular systems [45, 46]. Considering various aspects of semiempirical methods, PM7 was chosen for the optimization of the clusters of ILs. Then, the most stable structures were chosen and further calculated at the B3LYP-D3/6-31 +  $G^{**}$  level of theory. All the obtained structures were confirmed by frequency analysis to ensure the absence of imaginary frequencies.

In the ILs- $nH_2O$  system, the water molecules could form H-bonds with the Br<sup>-</sup> anion, oxygen, and azo positions of cations. Due to the high electronegativity and H-bonds acceptor of anion, the water molecules were put around the Br<sup>-</sup> anion, and then the water molecules around the oxygen and azo positions of cations were optimized at B3LYP-D3/6–31 + G<sup>\*\*</sup> level. The interaction energy of the [AzoC<sub>n</sub>DMEA]Br (n = 2,4,6,10) and ILs $nH_2O$  complexes were defined as two kinds of methods ( $\Delta E_1$  and  $\Delta E_2$ ):

$$\Delta E_1 = E (ILs_nH_2O) - [E (cation) + E (anion) + nE (H_2O)]$$
(1)

$$\Delta \mathbf{E}_2 = \mathbf{E} \left( ILs\_nH_2O \right) - \left[ \mathbf{E} \left( ILs \right) + nE \left( H_2O \right) \right]$$
(2)

Where  $E(ILs_nH_2O)$  is the electronic energy of ILs  $nH_2O$  complexes, E(cation) and E(anion) are the electronic energies of isolated cation and anion, respectively. E(ILs) and  $E(H_2O)$  are the electronic energies of ionic pairs and water molecules, respectively. For the interaction energy of  $\Delta E_1$ , the interaction energies of ILs were included and the data of  $\Delta E_1$  were stronger than that of  $\Delta E_2$ .

### **Analytical methods**

As useful methods to predict the reactive sites of the molecular surface, quantitative molecular surface analysis of electronic potential (ESP) and natural population analysis (NPA) charge have been widely used based on the electrochemical structure of reactants [47–49]. Zhang et al. [50] proposed an efficient evaluation of electronic potential with computerized optimized code in wavefunction analysis Multiwfn program [51, 52] which is freely available and become a useful tool for computational chemists. However, there is still potential to enhance evaluation efficiency through methods such as Schwarz screening, the utilization of explicit SIMD instructions, or the sharing of intermediates among various points. The ESP could be expressed by the equation as follows:

$$V_{tot}(r) = V_{nuc}(r) + V_{ele}(r)$$
  
=  $\sum_{A} \frac{Z_A}{|r - R_A|} - \int \frac{\rho(r')}{|r - r'|} dr'$  (3)

Where  $Z_A$  is the charge on the nucleus A located at  $R_A$ , and  $\rho(r)$  is the electronic density function of the molecule. ESP has been widely used for the prediction of nucleophilic and electrophilic sites as well as molecular recognition mode for a long time.

To generate an isodensity surface of volume in the computer graphics realm, the Marching Cubes (MC) approach [53] was the most popular, but there are some drawbacks to MC approach such as the ambiguity problem and lengthy looking-up tables. For the Van der Waals volume defined by Bader, Lu et al. proposed Marching Tetrahedra (MT) approach which is the extension of MC to accurately generate vertices and construct an electron density of 0.001 isosurface on the molecular surface [54].

The highest occupied orbital (HOMO), lowest unoccupied orbital (LUMO), and their energy level difference are commonly utilized to assess electron transfer properties and chemical reactivity [55]. The brand gap energy is defined as the following:

$$E_{gap} = E_{LUMO} - E_{HOMO} \tag{4}$$

Where the  $E_{LUMO}$  and  $E_{HOMO}$  are the HOMO and LUMO electronic energies, respectively.

Furthermore, the symmetry-adapted perturbation theory (SAPT) [56] was made to decompose the interaction energies of the  $[AzoC_2DMEA]Br-nH_2O$  ( $1 \le n \le 5$ ) complexes at the SAPT2+/aug-cc-pVDZ level [57, 58] which had been verified an outstanding performance for the majority of non-covalent complexes by using Psi4 program [59]. The interaction energies could be further separated into four components and defined as follows:

$$\Delta E_2 = E_{els} + E_{ex} + E_{ind} + E_{disp}, \ kcal/mol \quad (5)$$

Where the  $E_{els}$ ,  $E_{ex}$ ,  $E_{ind}$ , and  $E_{disp}$  are the classic electrostatic interaction, exchange repulsion term, induction term, and dispersion energy, respectively.

To better understand the nature of interactions in ILs and ILs-water clusters, the bond characteristics for the relevant configurations were also illustrated based on quantum theory of atoms in molecules (AIM) analysis [60, 61]. As a new method for visualizing the interactions in chemical systems, independent gradient model based on Hirshfeld partition (IGMH) function combined with sign( $\lambda_2$ ) $\rho$  was used to distinguish H-bonds interactions from other weak interactions [62]. The topological properties were analyzed with Multiwfn program with the wave functions generated from B3LYP-D3/6–31 + G<sup>\*\*</sup> calculations. All three analysis methods have been prevalently and successfully used in ionic liquid systems [63, 64].

### **Results and discussion**

Cations

### Quantitative molecular surface analysis of electronic potential analysis

The ESP surfaces of different alkyl chain lengths of  $[AzoC_nDMEA]^+$  cations were collected in Fig. 2 and area percentages in each ESP range had been listed in Figure S1-2. As shown in Fig. 2, the maximum and minimum ESP of [AzoC<sub>n</sub>DMEA]<sup>+</sup> cations are mainly located around the ammonium and azo groups, respectively. The minimum and maximum electronic potentials of trans and cis structures of [AzoC<sub>n</sub>DMEA]<sup>+</sup> cations are listed in Fig. 3, the minimum electronic potentials of trans- structures of [AzoC<sub>n</sub>DMEA]<sup>+</sup> (*n* = 2,4,6,10) are 17.56, 9.27, 3.64 and - 3.24 kcal/mol, respectively. With the increasing lengths of alkyl chain, the minimum and maximum ESP decrease. But the maximum of ESP will not change so obvious than that of minimum, due to the maximum electronic potentials of *trans*- structures of  $[AzoC_nDMEA]^+$  (*n* = 2,4,6,10) are 115.26, 115.10, 114.37, and 113.44 kcal/mol, respectively. Compared with minimum/maximum ESP of transand *cis*- structures of [AzoC<sub>n</sub>DMEA]<sup>+</sup> cations, taking the [AzoC<sub>2</sub>DMEA]<sup>+</sup> for an example, the minimum ESP of trans and cis- structures are 17.56 and -2.38 kcal/mol, respectively. The maximum ESP of trans- and cis-structures are 115.26 and 116.25 kcal/mol, respectively. Therefore, the minimum ESP of *cis*-structures is smaller than that of trans-, and the maximum ESP of cis-structures is larger than that of trans-. These differences could render different properties of azobenzene-based ionic liquids.

### Molecular volume of cations

Li et al. reported the smaller-sized aggregates of *trans*-isomer azobenzene-based ILs will grow up into



**Fig. 2** The electrostatic potential on the van der Waals surfaces of (**a**)  $trans-[AzoC_2DMEA]^+$  (**b**)  $trans-[AzoC_4DMEA]^+$  (**c**)  $trans-[AzoC_6DMEA]^+$  (**d**)  $trans-[AzoC_{10}DMEA]^+$  and (e)  $cis-[AzoC_2DMEA]^+$  (**f**)  $cis-[AzoC_4DMEA]^+$  (**g**)  $cis-[AzoC_6DMEA]^+$  (**h**)  $cis-[AzoC_{10}DMEA]^+$  structures of  $[AzoC_nDMEA]^+$  cations. (n = 2,4,6,10). The orange and cyan spheres represent the position of maximum and minimum points of ESP on the surface, respectively. (The units are kcal/mol)



**Table 1** The molecular dimension [azocndmea]+f [Azo $C_{[azocndmea]+}[azocndmea]+]^+$  ([azocndmea]+= 2,4,6,10) cationsbased [azocndmea]+ [azocndmea]+T approach (unit Å)

|                               |        | _     |       |                             | '                   |
|-------------------------------|--------|-------|-------|-----------------------------|---------------------|
|                               | Length | Width | Hight | Volume<br>(Å <sup>3</sup> ) | Surface<br>Area (Ų) |
| trans-AzoC <sub>2</sub> DMEA  | 21.77  | 8.39  | 6.69  | 414.21                      | 379.01              |
| trans-AzoC <sub>4</sub> DMEA  | 24.24  | 8.77  | 6.78  | 461.37                      | 421.52              |
| trans-AzoC <sub>6</sub> DMEA  | 26.73  | 9.06  | 6.79  | 508.71                      | 464.06              |
| trans-AzoC <sub>10</sub> DMEA | 31.72  | 9.45  | 6.79  | 603.66                      | 549.14              |
| cis-AzoC <sub>2</sub> DMEA    | 18.43  | 9.24  | 6.86  | 413.19                      | 372.41              |
| cis-AzoC <sub>4</sub> DMEA    | 20.96  | 9.40  | 6.88  | 460.32                      | 414.82              |
| cis-AzoC <sub>6</sub> DMEA    | 23.51  | 9.50  | 6.91  | 507.64                      | 457.30              |
| cis-AzoC <sub>10</sub> DMEA   | 28.62  | 9.61  | 6.93  | 602.57                      | 542.33              |

**Fig. 3** The minimum/maximum electronic potentials of *trans*- and *cis*structures of  $[AzoC_nDMEA]^+$  cations. (n = 2,4,6,10)

*cis*-isomer with larger-sized aggregates after UV irradiation as determined by small-angle X-ray scattering measurements [36]. Therefore, it's also necessary to investigate the molecular size of the azobenzene-based ILs. Taking the *trans*- $[AzoC_2DMEA]^+$  cation for an example, the molecular volume was shown in Figure S3, the units of the molecular volume analyzed by *Multiwfn* program were Angstrom and Bohr (1 Bohr = 0.52918 Angstrom). The molecular size information of cations can be output directly by *Multiwfn* program. As shown in Table 1, we collected the molecular volume of  $[AzoC_nD-MEA]^+$  (n = 2,4,6,10) cations. Taking the *trans*-  $[AzoC_nD-MEA]^+$  (n = 2,4,6,10) cations as examples, the length of

cations is 21.77, 24.24, 26.73, and 31.72 Å, respectively. The length of  $[AzoC_n DMEA]^+$  (*n* = 2,4,6,10) cations will elongate with the increasing numbers of alkyl chains. The width and height changes of cations are not so obvious as those of length. The volume and surface area of the cations is also elongated with the increase of alkyl chain length. Taking the [AzoC<sub>2</sub>DMEA]<sup>+</sup> structure for an example, the volumes of trans- and cis- are 414.21 and 413.19 Å<sup>3</sup>, respectively. And the surface areas of *trans*and cis- are 379.01 and 372.41 Å<sup>2</sup>, respectively. Comparative analysis of structural dimensions between trans- and *cis*-  $[AzoC_nDMEA]^+$  (*n* = 2,4,6,10) cations, the volume and surface area of the trans- is larger than that of cis-. From the microscopic perspective, the molecular volume of *cis*- is smaller, while the macroscopic aggregates are larger. This observation suggests that the aggregation mechanisms of ILs are not primarily governed by molecular-scale dimensions but rather by emergent macroscopic interaction complexities.

### **lonic** pairs

### Geometry and interaction energy

To investigate the microscopic interactions of ionic pairs, the structures of azobenzene-based ILs were optimized at the B3LYP-D3/6–31+G<sup>\*\*</sup> level. According to the anions were more easily to attack the most positive area of the cations, the Br<sup>-</sup> was initially put around the ammonium group of the  $[AzoC_nDMEA]^+$  cations. To assess the impact of alkyl chain length on these interactions, similar initial positions for Br<sup>-</sup> and cations in  $[AzoC_nDMEA]$  Br ILs were optimized at B3LYP-D3/6–31+G<sup>\*\*</sup> level. The *trans*- and *cis*-  $[AzoC_2DMEA]$ Br geometries and the interaction energies of  $[AzoC_nDMEA]$ Br (n = 2,4,6,10) are shown in Fig. 4. Additionally, the coordinates of *trans*- and *cis*-  $[AzoC_nDMEA]$ Br are collected in Table S1. Upon examining the structures of  $[AzoC_nDMEA]$ Br



**Fig. 4** The interaction energies (kcal/mol) of *trans*- and *cis*- structures of  $[AzoC_nDMEA]Br$  (n = 2,4,6,10)

ILs, it is evident that multiple H-bonds can be formed between the Br<sup>-</sup> anion and  $[AzoC_nDMEA]^+$  cations. The interaction energies of *trans*-structures of  $[AzoC_nD-MEA]Br$  (n = 2,4,6,10) are -100.12, -100.23, -99.68, and -98.93 kcal/mol, respectively. Therefore, the interaction energy will decrease with the increasing number of alkyl chains. Taking the  $[AzoC_2DMEA]Br$  for an example, the interaction energy of *trans*- is -100.12 kcal/mol which is weaker than that of *cis*- (-100.81 kcal/mol) in the similar position geometry, due to the maximum ESP of *cis*- structure (116.25 kcal/mol) larger than that of *trans*-(115.26 kcal/mol) as discussed above.

### Atom in molecules analysis

To investigate the interactions between cations and anions, topological analysis of the ILs was performed by the Bader's "atom in molecules" theory which has been widely and successfully used in many DFT calculations [60, 61]. A set of criteria for  $\rho_{BCP}$  and  $\bigtriangledown^2 \rho_{BCP}$  criteria are proposed for conventional H-bonds at the critical point (BCPs). The closed-shell interaction is positive in the range 0.002–0.035 a.u. for  $\rho_{BCP}$  and 0.024–0.139 a.u. for  $\nabla^2 \rho_{BCP}$  [65]. For the observed conformer, the  $\rho_{BCP}$  and  $\nabla^2 \rho_{BCP}$  values for of H-bonds fall within 0.0103–0.0205 a.u. and 0.0269-0.0564 a.u., respectively. The values of electron density ( $\rho_{BCP}$ ), Laplacian of the electron density  $(\nabla^2 \rho_{BCP})$ , energy density (H<sub>BCP</sub>), and potential energy density (V(r)) for the intermolecular H-bonds in transand *cis*- structures of  $[AzoC_nDMEA]Br$  (n = 2,4,6,10) ILs were summarized in Table 2 and the corresponding bonds labels could be found when the coordinates (Table S1) were imported into visualization software such as VMD, Avogadro and GaussView, etc. From the geometry of ILs, plenty of H-bonds could be formed between the Br- and the ammonium group of cations. Taking the *trans*- [AzoC<sub>2</sub>DMEA]Br for an example, the  $\rho_{BCP}$  of Br... H34-C33 and Br...H46-O45 are 0.0202 and 0.0128 a.u., respectively. The strength of Br...H34-C33 bond is stronger than that of Br...H46-O45. The multiple H-bonds formed between the [AzoC<sub>n</sub>DMEA]<sup>+</sup> cations and the Br<sup>-</sup> anion can stabilize the ILs structures. The  $\rho_{BCP}$  of Br...H29-C27 in *trans*-  $[AzoC_nDMEA]^+$  (*n* = 2,4,6,10) cations are 0.0113, 0.0114, 0.0107 and 0.0103 a.u., respectively. As the alkyl chain length increases, the strength of H-bonds would be decreased. It could be also confirmed by the interaction energies of ILs calculated above. Therefore, it could be concluded that multiple H-bonds can be formed between the cations and Br<sup>-</sup>. Besides, the strength of H-bonds formed between the cations and Br<sup>-</sup> would be decreased as the increasing number of the length of the alkyl chain.

**Table 2** The electron density ( $\rho_{BCP}$ ), laplacian of the electron density ( $\nabla^2 \rho_{BCP}$ ), energy density ( $H_{BCP}$ ), and potential energy density (V(r)) for *trans*- and *cis*- structures of [AzoC<sub>n</sub>DMEA]Br (n = 2,4,6,10) ILs (a.u.)

| Structure                                 | H-Bond    | ρ <sub>BCP</sub> | $\nabla^2 \rho_{BCP}$ | H <sub>BCP</sub> (10 <sup>-3</sup> ) | V( <i>r</i> ) |
|-------------------------------------------|-----------|------------------|-----------------------|--------------------------------------|---------------|
| <i>trans-</i> [AzoC <sub>2</sub> DMEA]Br  | BrH29-C27 | 0.0113           | 0.0295                | 0.9310                               | -0.0055       |
|                                           | BrH44-C39 | 0.0185           | 0.0461                | 0.5710                               | -0.0104       |
|                                           | BrH34-C33 | 0.0202           | 0.0562                | 0.8939                               | -0.0123       |
|                                           | BrH46-O45 | 0.0128           | 0.0325                | 0.7275                               | -0.0067       |
| <i>trans-</i> [AzoC <sub>4</sub> DMEA]Br  | BrH51-C50 | 0.0114           | 0.0295                | 0.9050                               | -0.0056       |
|                                           | BrH44-C39 | 0.0181           | 0.0454                | 0.6218                               | -0.0101       |
|                                           | BrH34-C33 | 0.0203           | 0.0562                | 0.8631                               | -0.0123       |
|                                           | BrH46-O45 | 0.0126           | 0.0321                | 0.7338                               | -0.0065       |
| <i>trans-</i> [AzoC <sub>6</sub> DMEA]Br  | BrH58-C57 | 0.0107           | 0.0279                | 0.8963                               | -0.0052       |
|                                           | BrH44-C39 | 0.0180           | 0.0451                | 0.6308                               | -0.0100       |
|                                           | BrH34-C33 | 0.0204           | 0.0563                | 0.8367                               | -0.0124       |
|                                           | BrH46-O45 | 0.0128           | 0.0324                | 0.7141                               | -0.0067       |
| <i>trans-</i> [AzoC <sub>10</sub> DMEA]Br | BrH71-C69 | 0.0103           | 0.0269                | 0.8890                               | -0.0049       |
|                                           | BrH44-C39 | 0.0179           | 0.0449                | 0.6374                               | -0.0099       |
|                                           | BrH34-C33 | 0.0205           | 0.0563                | 0.8213                               | -0.0124       |
|                                           | BrH46-O45 | 0.0130           | 0.0327                | 0.6985                               | -0.0068       |
| <i>cis</i> - [AzoC <sub>2</sub> DMEA]Br   | BrH29-C27 | 0.0112           | 0.0293                | 0.9289                               | -0.0055       |
|                                           | BrH42-C39 | 0.0186           | 0.0462                | 0.5628                               | -0.0104       |
|                                           | BrH34-C33 | 0.0204           | 0.0564                | 0.8695                               | -0.0124       |
|                                           | BrH46-O45 | 0.0128           | 0.0324                | 0.7292                               | -0.0066       |
| <i>cis</i> - [AzoC <sub>4</sub> DMEA]Br   | BrH52-C51 | 0.0114           | 0.0295                | 0.9033                               | -0.0056       |
|                                           | BrH42-C39 | 0.0181           | 0.0454                | 0.6180                               | -0.0101       |
|                                           | BrH34-C33 | 0.0204           | 0.0563                | 0.8562                               | -0.0124       |
|                                           | BrH46-O45 | 0.0126           | 0.0319                | 0.7385                               | -0.0065       |
| <i>cis-</i> [AzoC <sub>6</sub> DMEA]Br    | BrH58-C57 | 0.0108           | 0.0282                | 0.8977                               | -0.0053       |
|                                           | BrH42-C39 | 0.0179           | 0.0450                | 0.6362                               | -0.0100       |
|                                           | BrH34-C33 | 0.0204           | 0.0563                | 0.8404                               | -0.0124       |
|                                           | BrH46-O45 | 0.0127           | 0.0321                | 0.7254                               | -0.0066       |
| <i>cis</i> - [AzoC <sub>10</sub> DMEA]Br  | BrH70-C69 | 0.0103           | 0.0269                | 0.8892                               | -0.0049       |
|                                           | BrH42-C39 | 0.0179           | 0.0449                | 0.6363                               | -0.0100       |
|                                           | BrH34-C33 | 0.0205           | 0.0564                | 0.8202                               | -0.0125       |
|                                           | BrH46-O45 | 0.0130           | 0.0326                | 0.7011                               | -0.0068       |

### Frontier molecular orbital analysis

To investigate the chain length and trans-/cis- structures on the electronic properties of [AzoC<sub>n</sub>DMEA]Br (n=2,4,6,10), the frontier molecular orbital analysis of the ILs was conducted for these ILs in this section. The distribution maps of HOMO and LUMO energies projected on the van der Waals surface for trans- and cis- $[AzoC_nDMEA]Br$  (*n* = 2,4,6,10) are shown in Figure S4, where the positive and negative phases of the orbital wave functions are color-coded in red and blue, respectively. The orbital distribution at the HOMO level is predominantly delocalized across the N = N bonds and the cyclobenzene ring of the azobenzene moiety, whereas the orbital distribution at the LUMO level is primarily localized within the Br<sup>-</sup> ion. The distribution centers of the HOMO and LUMO orbitals remain unchanged as the length of the alkyl chain increases. The  $E_{HOMO}$ , E<sub>LUMO</sub>, and gap are collected in Fig. 5. Taking the trans- $[AzoC_nDMEA]Br$  (*n* = 2,4,6,10) as an example, the  $E_{HOMO}$  are -125.99, -125.33, -124.40, and -123.37 kcal/mol, respectively. The  $E_{LUMO}$  are -61.60, -57.88, -56.16, and -54.56 kcal/mol, respectively. Besides, the gap energies are 64.39, 67.45, 68.24, and 68.82 kcal/mol, respectively. Therefore, as the alkyl chain lengthens, the activity of [AzoC<sub>n</sub>DMEA]Br (n=2,4,6,10) will decrease due to the increasing gap energies. Compared with the *trans-* and *cis-* structures of [AzoC<sub>n</sub>DMEA]Br (n=2,4,6,10), the gap energies of *trans-* and *cis-*[AzoC<sub>2</sub>DMEA]Br are 64.39 and 69.85 kcal/mol. The *trans-*structures of [AzoC<sub>n</sub>DMEA]Br (n=2,4,6,10) are more prone to excitation than their corresponding *cis-* structures.

### lonic clusters (*n*Ls, $1 \le n \le 4$ )

### Geometry and interaction energy

Ion clusters formed by the interconnection of multiple ions can provide insights into the arrangement of ions within the bulk phase of ILs [66, 67]. The ionic pair is the threshold to investigate the ionic clusters and the ion



**Fig. 5** Energy level diagram (HOMO and LUMO energies and HOMO-LUMO energy gaps) of *trans*- and *cis*- structures of  $[AzoC_nDMEA]Br$  (n = 2,4,6,10)

clusters can describe the structures of bulk ionic liquids and aqueous solutions [68]. Due to the repetitive calculations and wide use of [AzoC2DMEA]Br, we take the [AzoC<sub>2</sub>DMEA]Br as an example, different numbers of trans- and cis-  $n[AzoC_2DMEA]Br$  ( $1 \le n \le 4$ ) ionic clusters were explored in this part. The optimized structures and the relative energies of different trans- and *cis-* n[AzoC<sub>2</sub>DMEA]Br (1 ≤ n ≤ 4) ionic clusters at the PM7 level are listed in Figure S5-S6. The interaction energies of the most stable *trans-* and *cis- n*[AzoC<sub>2</sub>DMEA]Br  $(1 \le n \le 4)$  clusters were collected in Table 3. Taking the interaction energies of trans- and cis- 4[AzoC2DMEA]Br for example, the  $\triangle E_1$  of *trans*- and *cis*- are - 551.84 and -501.30 kcal/mol, respectively. The interaction energies of trans- clusters are stronger than those of cis- clusters based on the DFT calculations. It can be also speculated that the interaction energies of  $\triangle E_2$  are smaller than those of  $\triangle E_1$  because the interaction energies of anions-cations have been excluded. The interaction energies of per ion pair of *trans- n*[AzoC<sub>2</sub>DMEA]Br are – 27.07, -35.21, and -44.00 kcal/mol, when n = 2, 3, and 4. Per ion pair of cation-anion interaction energy has a decreasing trend with the increasing numbers of water molecules, but the energies of clusters with the number of ion pairs displayed a trend to saturation for ethylammonium hydrogen sulfate protic ILs [69] and  $-SO_3H$  functionalized ILs [70] reported before.

## Independent gradient model based on Hirshfeld partition (IGMH) analysis

As a practical tool for investigating non-covalent interactions, independent gradient model based on Hirshfeld partition has been widely used in the visual analysis of intramolecular and intermolecular interactions [62]. To gain a more detailed understanding of the interactions, taking the 2[AzoC<sub>2</sub>DMEA]Br clusters as an example, the visualization of these inter-molecular interactions of the most stable structures explored by the Molclus program of the trans- and cis- 2[AzoC2DMEA]Br clusters were shown in Fig. 6. The interaction energy  $(\Delta E_1)$  of *trans*-2[AzoC<sub>2</sub>DMEA]Br cluster is -242.05 kcal/mol, which is stronger than that of cis- structure (-210.14 kcal/mol). From Fig. 6, it could be found that multiple H-bonds could be formed between the anions and cations, the Br- mainly interacts with the ammonium group and the hydroxyl groups of the cations. Additionally,  $\pi$ -stacking interactions among the azobenzene moieties constitutes the primary interaction mode among the cations. The quasi-3D H-bonds network is formed in the ILs clusters to modulate the trans- and cis-isomerism of the photoresponsive ILs.

### Interactions between ILs and $nH_2O$ ( $1 \le n \le 5$ ) Geometry and interaction energy

The aggregation behavior of the azobenzene-based ionic liquids would be formed in water and the concentration-dependent conductivity of aqueous ILs changes before and after UV irradiation [36]. We have studied the impact of different numbers of water molecules on cisand trans-structures of ILs by using the same approach. Figure 7 shows the optimized structures of the two binary complex systems (trans- and cis-[AzoC<sub>2</sub>DMEA] Br with water). To compare the roles of water molecules, the water molecules were added to the ionic pairs one by one based on the previously optimized structures. Their interaction energies (E<sub>int</sub>) of ILs and water molecules ([AzoC<sub>2</sub>DMEA]Br-*n*H<sub>2</sub>O complexes) are listed in Table 4. Taking the trans-[AzoC2DMEA]Br-H2O structure for an example, the  $\Delta E_1$  and  $\Delta E_2$  values are  $-\,116.85$  and – 16.73 kcal /mol, respectively. The  $\Delta E_1$  was stronger than that of  $\Delta E_2$ , due to the interaction energies of ionic liquids were included. Furthermore, the interaction energies

Table 3 Interaction energy (kcal/mol) of trans- and cis-  $n[AzoC_2DMEA]Br$  ( $1 \le n \le 4$ ) optimized at B3LYP-D3/6-31 + G\*\*//PM7 level

|                             | $\Delta E_{1,trans}$ | ΔE <sub>1/cis</sub> | ΔE <sub>2/trans</sub> | ΔE <sub>2′cis</sub> | $\Delta E_{2'trans}/n$ | ΔE <sub>2/cis</sub> /n |
|-----------------------------|----------------------|---------------------|-----------------------|---------------------|------------------------|------------------------|
| [AzoC <sub>2</sub> DMEA]Br  | -93.96               | -81.30              | 0                     | 0                   | -                      | -                      |
| 2[AzoC <sub>2</sub> DMEA]Br | -242.05              | -210.14             | -54.14                | -47.54              | -27.07                 | -23.77                 |
| 3[AzoC <sub>2</sub> DMEA]Br | -387.51              | -344.43             | -105.64               | -100.52             | -35.21                 | -50.26                 |
| 4[AzoC <sub>2</sub> DMEA]Br | -551.84              | -501.30             | -176.01               | -176.08             | -44.00                 | -88.04                 |



Fig. 6 Intermolecular interaction isosurface (s = 0.007 a.u.) of (a) *trans*- 2[AzoC<sub>2</sub>DMEA]Br and (b) *cis*- 2[AzoC<sub>2</sub>DMEA]Br. Blue indicates strong attractive interaction, green indicates the van der Walls interaction and red indicates the steric effect



Fig. 7 The optimized (a-f) trans- and (e-l) cis- structures of  $[AzoC_2DMEA]Br-nH_2O$  ( $0 \le n \le 5$ ) at B3LYP-D3/6-31+G<sup>\*\*</sup> level. H-bonds are indicated by dashed lines

**Table 4** Interaction energy (kcal/mol) of *trans*- and *cis*- [AzoC<sub>3</sub>DMEA]Br with  $nH_3O$  ( $0 \le n \le 5$ )

|                                              | ΔΕ       | ΔΕ      | ΔΕ     | ΔΕ     | ΔE <sub>2</sub> / <i>n</i> | ΔE <sub>nut</sub> /n |
|----------------------------------------------|----------|---------|--------|--------|----------------------------|----------------------|
|                                              | _100.1.2 | -100.81 |        |        | ==2/trans/                 | =-2/cis/**           |
|                                              | -100.12  | -100.01 | 0      | 0      |                            |                      |
| [AzoC <sub>2</sub> DMEA]Br-H <sub>2</sub> O  | -116.85  | -117.56 | -16.73 | -16.75 | -16.73                     | -16.75               |
| [AzoC <sub>2</sub> DMEA]Br-2H <sub>2</sub> O | -130.08  | -130.78 | -29.96 | -29.97 | -14.98                     | -14.99               |
| [AzoC <sub>2</sub> DMEA]Br-3H <sub>2</sub> O | -147.30  | -148.05 | -47.18 | -47.24 | -15.73                     | -15.75               |
| [AzoC <sub>2</sub> DMEA]Br-4H <sub>2</sub> O | -155.56  | -156.94 | -55.45 | -56.13 | -13.86                     | -14.03               |
| [AzoC <sub>2</sub> DMEA]Br-5H <sub>2</sub> O | -165.45  | -166.57 | -65.34 | -65.76 | -13.07                     | -13.15               |

 $(\Delta E_2)$  of *cis*- and *trans* -  $[AzoC_2DMEA]Br-H_2O$  are - 16.75 and - 16.73 kcal/mol, respectively. The calculated interaction energy of the *cis*- $[AzoC_2DMEA]Br-nH_2O$  is stronger than that of *trans*- $[AzoC_2DMEA]Br-nH_2O$  ( $1 \le n \le 5$ ) which is consistent with the other photoresponsive ILs reported research [71, 72]. The interaction energies ( $E_{2^{n}trans}$ ) of [AzoC<sub>2</sub>DMEA]Br with  $nH_2O$  ( $1 \le n \le 5$ ) are -16.73, -29.96, -47.18, -55.45 and -65.34 kcal/mol, respectively. As the number of water molecules increases, the interaction energies rise accordingly. The values of



Fig. 8 Energy decomposition of interaction energies (in kcal/mol) for the (a) trans- and (b) cis-  $[AzoC_2DMEA]Br-nH_2O(1 \le n \le 5)$ 

 $\Delta E_{2,\text{trans}} / n$ , and  $\Delta E_{2,\text{ cis}} / n$  will decrease with the increasing numbers of water molecules and then do not change so obviously at n = 4 and n = 5 around 13 kcal/mol. The energy contribution per water molecule within the ILs-water clusters tends towards saturation as the number of water molecules continues to grow.

### Symmetry-adapted perturbation theory analysis

The energy decomposition analyses of cis/trans structures of  $[AzoC_2DMEA]Br-nH_2O$   $(1 \le n \le 5)$  are shown in Fig. 8. Taking the cis- [AzoC<sub>2</sub>DMEA]Br-H<sub>2</sub>O for an example, the electrostatic interaction, exchange repulsion term, induction term, and dispersion energy are -20.34, 16.95, -5.84, and -4.84 kcal/mol, respectively. The electrostatic interaction and exchange repulsion term account for a large proportion of the total interaction energy, approximately 42.40% and 35.33%, respectively. Therefore, the electrostatic interaction plays a critical role in the stabilization of ILs and water structures. With the increasing numbers of water molecules, the electrostatic interaction of *cis*-  $[AzoC_2DMEA]Br-nH_2O$   $(1 \le n \le 5)$ are - 20.34, -32.42, -56.89, -69.63, and - 80.05 kcal/mol, respectively. Both the electrostatic interaction, exchange repulsion term, induction term, and dispersion energy had an increasing tendency. However, the occupation of different interaction terms maintains the stability with the sequence: electrostatic interaction > exchange repulsion>induction>dispersion energy. The difference in energy decomposition of trans- and cis-[AzoC2DMEA]

Br- $nH_2O$  ( $1 \le n \le 5$ ) was not so obvious, due to the small differences in their total interaction energies.

### Conclusion

Density functional theory (DFT) calculations have been employed to investigate the geometries and properties of cations, ionic pairs, ionic clusters, as well as ILs/ water clusters. As the length of the alkyl chain increases, both the minimum and maximum electrostatic potential (ESP) will decrease. The active site of the cations is predominantly situated around the ammonium group. The volume and surface area of the *cis*- [AzoC<sub>n</sub>DMEA]<sup>+</sup> (n=2,4,6,10) cations are smaller compared to those of their trans- structures. Multiple H-bonds can be formed between the Br<sup>-</sup> anion and [AzoC<sub>n</sub>DMEA]<sup>+</sup> cations to stabilize the ILs structures and the anion primarily interacting with the ammonium group of cations. With the increase of alkyl chain length, the interaction energies have a decreasing trend. The interaction energies of *trans-* n[AzoC<sub>2</sub>DMEA]Br (1 ≤ n ≤ 4) clusters are stronger than that of cis-. From the interaction of ILs/water systems, the interaction energy between *trans*- structures of photoresponsive ILs and water molecules is lesser than that of cis-. The energies of per water molecules of the ILs-waters clusters would tend to saturation with the increasing number of water molecules. Electrostatic interactions play a pivotal role in stabilizing the structures of ILs and water, thereby modulating their aggregation behavior. This work provides new insights into the molecular level structure and photoresponsive characteristics/aggregation behavior of the azobenzene-based ILs and may be useful for the design of more novel photosensitive ILs.

### **Supplementary Information**

The online version contains supplementary material available at https://doi.or g/10.1186/s13065-025-01433-1.

Supplementary Material 1

Supplementary Material 2

### Acknowledgements

The work was carried out at Shanxi Supercomputing Center of China, and the calculations were performed on TianHe-2. We thank the great support for computing of Shanxi Supercomputing Center of China.

### Author contributions

Liyao Ying: drafted the manuscript and performed the data analysis. Zhaoyang Ju: reviewed and edited the manuscript and funding acquisition. Chunjin Lin: reviewed and edited the manuscript. Pin Wang: reviewed and edited the manuscript. Haixiang Cheng: collected the data and verified the analytical methods. Liyong Ding: reviewed and edited the manuscript. Tianshu Chu: reviewed and edited the manuscript. Chunxiao Gong: reviewed and edited the manuscript. Bing Zhou: reviewed and edited the manuscript. MengtingYu: designed and reviewed the manuscript. Chengsheng Ge: reviewed the manuscript and designed the study.

#### Funding

This research was supported by the Joint Funds of the Zhejiang Provincial Natural Science Foundation of China under Grant No. LZY24B030001, the National Natural Science Foundation of China under Grant No. 22408210, the National College Students' Innovation and Entrepreneurship Training Program Grant No. 202411488035, and the Research Fund for the Program of "Xinmiao" (Potential) Talents in Zhejiang Province under Grant No. 2024R43A001.

#### Data availability

The datasets used and/or analysed during the current study are available from the corresponding author on reasonable request.

### Declarations

**Ethics approval and consent to participate** Not applicable.

### **Consent for publication**

Not applicable.

### **Competing interests**

The authors declare no competing interests.

Received: 2 January 2025 / Accepted: 25 February 2025 Published online: 10 March 2025

### References

- 1. Bhatnagar A, Wagh S, Singh B, Agrawal RR, Khan F. Smart materials-a review. 2016.
- Lee HP, Gaharwar AK. Light-responsive inorganic biomaterials for biomedical applications. Adv Sci (Weinh). 2020;7(17):2000863. https://doi.org/10.1002/ad vs.202000863.
- Zardehi-Tabriz A, Ghayebzadeh Y, Gerdroodbar AE, Golshan M, Roghani-Mamaqani H, Salami-Kalajahi M. Polyampholyte Polymers-Based sensors: A review on stimuli and applications. Macromol Mater Eng. 308;2023.
- Xia X, Afshar A, Yang H, Portela CM, Kochmann DM, Di Leo CV, Greer JR. Electrochemically reconfigurable architected materials. Nature. 2019;573:205–13.

- Eastoe J, Vesperinas A. Self-assembly of light-sensitive surfactants. Soft Matter. 2005;1:338–47.
- Chu Z, Dreiss, Cécile A. Feng, Yujun, smart wormlike micelles. Chem Soc Rev. 2013;42:7174–203.
- Yuan X, Li Z, Feng Y, Pei Y, Wang H, Liu D, Wang D, Wang J. Phase behavior and microstructure of Azobenzene ionic liquids based photo-responsive microemulsions. J Mol Liq. 2019;277:805–11.
- Ran H, Wang J, Abdeltawab AA, Chen X, Yu G, Yu Y. Synthesis of polymeric ionic liquids material and application in CO2 adsorption. J Energy Chem. 2017;26:909–18.
- Shi K, Guo L, Zheng R, Wang H, Chen Y. Preparation of Diacid comprising ionic liquid catalyst and its application in catalytic degradation of PET. Catal Lett. 2021;152:1182–93.
- Cheng DH, Chen XW, Shu Y, Wang JH. Selective extraction/isolation of hemoglobin with ionic liquid 1-butyl-3-trimethylsilylimidazolium hexafluorophosphate (BtmsimPF6). Talanta. 2008;75:1270–8.
- Jiang K, Zhou G, Fang T, Liu X. Permeability of vesicles for Imidazolium-Based ionic liquids in aqueous solution: A molecular dynamic simulation study. Ind Eng Chem Res. 2021;60:3174–83.
- Wang YL, Li B, Sarman S, Mocci F, Lu ZY, Yuan J, Laaksonen A. Fayer, microstructural and dynamical heterogeneities in ionic liquids. Chem Rev. 2020;120:5798–877.
- Pessoni L, Siniscalco D, Boussonnière A, Castanet A-S, Billon L, Delorme N. Photo-reversible solid to liquid transition of Azobenzene containing polymers: impact of the chemical structure and chain length. Eur Polymer J. 2022;174:111297.
- Chen YF, Huang MR, Hsu YS, Chang MH, Lo TY, Gautam B, Hsu HH, Chen JT. Photo-Healable Fabrics: Achieving Structural Control via Photochemical Solid–Liquid Transitions of Polystyrene/Azobenzene-Containing Polymer Blends, ACS Applied Materials & Interfaces. 2024.
- Weis P, Hess A, Kircher G, Huang S, Auernhammer GK, Koynov K, Butt HJ, Wu S. Effects of spacers on photoinduced reversible Solid-to-Liquid transitions of Azobenzene-Containing polymers. Chemistry. 2019;25:10946–53.
- Han J, Zheng Q, Jin C, Wang S, Liu Y, Zhao Y, Zhu J. Comparative study on properties, structural changes, and isomerization of Cis/Trans-Stilbene under high pressure. J Phys Chem C. 2022;126:16859–66.
- Tamura H, Shinohara Y, Arai T. Synthesis and photochemistry of Stilbene ionic liquids. Chem Lett. 2010;39:240–1.
- Hou L, Leydecker T, Zhang X, Rekab W, Samorì P. Engineering optically switchable transistors with improved performance by controlling interactions of diarylethenes in polymer matrices. XXXX: Journal of the American Chemical Society; 2020.
- 20. Wu N, Yam V. Photochromic barbiturate Pendant-containing Benzo[b]phosphole oxides with Co-assembly property. And Photoinduced Morphological Changes. 2019.
- Li L, Peng C, Xu Q, Chen S, He Y, Xu W, Jiang J. The mechanoresponsive self-assembly of spiropyran doped films with dual sensitivity. Mater Lett. 2018;214:150–3.
- Das G, Prakasam T, Alkhatib N, AbdulHalim RG, Chandra F, Sharma SK, Garai B, Varghese S, Addicoat MA, Ravaux F, Pasricha R, Jagannathan R, Saleh Ni, Kirmizialtin S, Olson MA, Trabolsi A. Light-driven self-assembly of spiropyranfunctionalized covalent organic framework. Nat Commun. 2023;14:3765.
- Cao Z, Liu H, Jiang L. Hydrogen-Bonding-Driven tough ionogels containing Spiropyran-Functionalized ionic liquids. ACS Appl Polym Mater. 2020;2:2359–65.
- Fihey A, Perrier A, Browne WR, Jacquemin D. Multiphotochromic molecular systems. Chem Soc Rev. 2015;44:3719–59.
- Li Z, Feng Y, Yuan X, Wang H, Zhao Y, Wang J. Photo-Triggered reversible phase transfer of Azobenzene-Based ionic liquid surfactants between oil and water. Int J Mol Sci. 20;2019.
- Ma X, Lan X, Wu L, Wang L, Gu Q, Shi Y, Gu X, Luo Z. Photo-induced actuator using temperature and light dual responsive Azobenzene containing ion gel in ionic liquid. Eur Polymer J. 123;2020.
- 27. Canongia Lopes JNA, Pádua AAH. Nanostructural organization in ionic liquids. J Phys Chem B. 2006;110:3330–5.
- Bhargava B.L., Balasubramanian S. Refined potential model for atomistic simulations of ionic liquid [bmim][PF6]. J Chem Phys. 2007;127:2071.
- Znamenskiy V, Kobrak MN. Molecular dynamics study of polarity in roomtemperature ionic liquids. J. Phys. Chem. B 2004;108(46):17194–7.

- Li J, Yang Y, Zhang D. DFT study of Fructose dehydration to 5-hydroxymethylfurfural catalyzed by imidazolium-based ionic liquid. Chem Phys Lett. 2019;723:175–81.
- 31. Zhang Y, He H, Dong K, Fan M, Zhang S. A DFT study on lignin dissolution in imidazolium-based ionic liquids. RSC Adv. 2017;7:12670–81.
- 32. Sun H, Cao B, Tian Q, Liu S, Du D, Xue Z, Fu H. A DFT study on the absorption mechanism of vinyl chloride by ionic liquids. J Mol Liq. 2016;215:496–502.
- Zheng Y, Dai Y, Hong Y, Dai S, Wang C, Cai Y, Wang K. Alkyl chain length affecting the structure and interactions of choline-based amino acid ionic liquids: insights from a computational study. J Mol Liq. 2024;404:124972.
- Hu K, Zhang H, Kong M, Qin M, Ouyang M, Jiang Q, Wang G, Zhuang L. Effect of alkyl chain length of imidazolium cations on foam properties of anionic surface active ionic liquids: experimental and DFT studies. J Mol Liq. 2021;340:117197.
- Yang J, Wang H, Wang J, Guo X, Zhang Y. Light-modulated aggregation behavior of some unsubstituted cinnamate-based ionic liquids in aqueous solutions. RSC Adv. 2015;5:96305–12.
- Li Z, Wang H, Chu M, Guan P, Zhao Y, Zhao Y, Wang J. Photo-isomerization and light-modulated aggregation behavior of azobenzene-based ionic liquids in aqueous solutions. RSC Adv. 2017;7:44688–95.
- 37. Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Scalmani G, Barone V, Petersson GA, Nakatsuji H, Li X, Caricato M, Marenich AV, Bloino J, Janesko BG, Gomperts R, Mennucci B, Hratchian HP, Ortiz JV, Izmaylov AF, Sonnenberg JL, Williams F, Ding F, Lipparini F, Egidi J, Goings B, Peng A, Petrone T, Henderson D, Ranasinghe VG, Zakrzewski J, Gao N, Rega G, Zheng W, Liang M, Hada M, Ehara K, Toyota R, Fukuda J, Hasegawa M, Ishida T, Nakajima Y, Honda O, Kitao H, Nakai T, Vreven K, Throssell JA, Montgomery JE Jr., Peralta F, Ogliaro MJ, Bearpark JJ, Heyd EN, Brothers KN, Kudin VN, Staroverov TA, Keith R, Kobayashi J, Normand K, Raghavachari AP, Rendell JC, Burant SS, Iyengar J, Tomasi M, Cossi JM, Millam M, Klene C, Adamo R, Cammi JW, Ochterski RL, Martin. K. Morokuma, O. Farkas, J.B. Foresman, DJ. Fox, Gaussian 16 in, Wallingford, CT. 2016.
- Humphrey W, Dalke A, Schulten K. Visual molecular dynamics. J Mol Graph. 1996;14:33–8.
- Grimme S, Hujo W, Kirchner B. Performance of dispersion-corrected density functional theory for the interactions in ionic liquids. Phys Chem Chem Phys. 2012;14:4875–83.
- Grimme S, Antony J, Ehrlich S, Krieg H. A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu. J Chem Phys. 2010;132(15):154104. https://doi.org/10.1063/1. 3382344.
- Foadin CST, Nya FT, Ejuh GW, Malloum A, Conradie J, Ndjaka JM. DFT study of the influence of impurities on the structural, electronic, optoelectronic, and nonlinear optical properties of graphene nanosheet functionalized by the carboxyl group–COOH. J Mol Model. 2020;26:327.
- Wu T, Sun T, Ren Y, Zhang R. Molecular mechanism for the absorption of ketone volatile organic compounds by ionic liquids. Comput Theor Chem. 2024;1234:114545.
- 43. Lu T. Molclus program, Version 1.9.9.9. http://www.keinsci.com/research/molc lus.html. 2022.
- Soyemi A, Szilvási T. Benchmarking semiempirical QM methods for calculating the dipole moment of organic molecules. J Phys Chem A. 2022;126:1905–21.
- Sure R, Grimme S. Comprehensive benchmark of association (Free) energies of realistic Host–Guest complexes. J Chem Theory Comput. 2015;11:3785–801.
- Stewart JJP. Optimization of parameters for semiempirical methods VI: more modifications to the NDDO approximations and re-optimization of parameters. J Mol Model. 2013;19:1–32.
- 47. Fu R, Lu T, Chen F-W. Comparing methods for predicting the reactive site of electrophilic substitution. Acta Phys Chim Sin. 2014;30:628–39.
- Murray JS, Politzer P. Electrostatic potentials: chemical applications, in: encyclopedia of computational chemistry. John Wiley & Sons, Ltd. 2002.
- Wang Z, Liu Y, Zheng B, Zhou F, Jiao Y, Liu Y, Ding X, Lu T. A theoretical investigation on Cu/Ag/Au bonding in XH2P---MY(X = H. J Chem Phys. 2018;148:194106. CH3, F, CN, NO2; M = Cu, Ag, Au; Y = F, Cl, Br, I).
- Zhang J, Lu T. Efficient evaluation of electrostatic potential with computerized optimized code. Phys Chem Chem Phys. 2021;23:20323–8.

- Lu T, Chen F, Multiwfn. A multifunctional wavefunction analyzer. J Comput Chem. 2012;33:580–92.
- Lu T. A comprehensive electron wavefunction analysis toolbox for chemists, Multiwfn. J Chem Phys. 2024;161(8):082503. https://doi.org/10.1063/5.021627
  2.
- 53. Lorensen WE. Marching cubes: A hign resolution 3D surface construction algorithm, Computer Graphics (Proceedings of SIGGRAPH'87). 21;1987.
- 54. Lu T, Chen F. Quantitative analysis of molecular surface based on improved marching tetrahedra algorithm. J Mol Graph Model. 2012;38:314–23.
- 55. Puzari P, Swathi RS, Sarkar B, Adhikari S. A quantum-classical approach to the photoabsorption spectrum of pyrazine. J Chem Phys. 2005;123:77.
- Parker TM, Burns LA, Parrish RM, Ryno AG, Sherrill CD. Levels of symmetry adapted perturbation theory (SAPT). I. Efficiency and performance for interaction energies. J Chem Phys. 2014;140:094106.
- 57. Deng Z, Liu C, Li Z, Zhang Y. An efficient method by combining different basis sets and SAPT levels. J Comput Chem. 2024;45:1936–44.
- Hajji M, Abad N, Habib MA, Elmgirhi SMH, Guerfel T. Computational chemistry methods for modelling non-covalent interactions and chemical reactivity an overview. J Indian Chem Soc. 2021;98:100208.
- Turney JM, Simmonett AC, Parrish RM, Hohenstein EG, Evangelista FA, Fermann JT, Mintz BJ, Burns LA, Wilke JJ, Abrams ML, Russ NJ, Leininger ML, Janssen CL, Seidl ET, Allen WD, Schaefer HF, King RA, Valeev EF, Sherrill CD, Crawford TD. Psi4: an open-source Ab initio electronic structure program. WIREs Comput Mol Sci. 2012;2:556–65.
- 60. Saleh G, Gatti C, Lo L, Presti. Non-covalent interaction via the reduced density gradient: independent atom model vs experimental multipolar electron densities. Comput Theor Chem. 2012;998:148–63.
- 61. Lü R, Lin J, Qu Z. Theoretical study on interactions between ionic liquids and organosulfur compounds. Comput Theor Chem. 2012;1002:49–58.
- 62. Lu T, Chen Q. Independent gradient model based on Hirshfeld partition: A new method for visual study of interactions in chemical systems. J Comput Chem. 2022;43:539–55.
- Ma J, Yang X, Wang Y, Wang B. Electronic-level insight into the weak interactions of ion pairs in acetate anion-based ionic liquids. J Mol Liq. 2020;303:112668.
- 64. Ju Z, Yao X, Luo Z, Cao M, Xiao W. Theoretical studies on the noncovalent interaction of Fructose and functionalized ionic liquids. Carbohydr Res. 2020;487:107882.
- 65. Veillard A, Dediew A, Rohmer MM. Horizons of quantum chemistry. Horizons of Quantum Chemistry. 1980.
- Liu X, Zhou G, Zhang S. Molecular dynamics simulation of acyclic guanidinium-based ionic liquids. Fluid Phase Equilibria. 2008;272:1–7.
- 67. Wang Y, Voth GA. Unique Spatial heterogeneity in ionic liquids. J Am Chem Soc. 2005;127:12192–3.
- Dong K, Song Y, Liu X, Cheng W, Yao X, Zhang S. Understanding structures and hydrogen bonds of ionic liquids at the electronic level. J Phys Chem B. 2012;116:1007–17.
- Fedorova IV, Krestyaninov MA, Safonova LP. Structure of ethylammonium hydrogen sulfate protic ionic liquid through DFT calculations and MD simulations: the role of hydrogen bonds. Struct Chem. 2023;34:879–90.
- Yu M, Liu J, Cao X, Wei C, Liang H, Gong C, Ju Z. Structures and hydrogen bonds of -SO3H functionalized acid ionic liquids. J Mol Liq. 2024;406:125129.
- Pan A, Mati SS, Naskar B, Bhattacharya SC, Moulik SP. Self-Aggregation of MEGA-9 (N-Nonanoyl-N-methyl-d-glucamine) in aqueous medium: physicochemistry of interfacial and solution behaviors with special reference to formation energetics and micelle microenvironment. J Phys Chem B. 2013;117:7578–92.
- 72. Cheng N, Yu P, Wang T, Sheng X, Bi Y, Gong Y, Yu L. Self-Aggregation of new Alkylcarboxylate-Based anionic surface active ionic liquids: experimental and theoretical investigations. J Phys Chem B. 2014;118:2758–68.

### **Publisher's note**

Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.