

# Light controlled liquefactions of non-photoresponsive crystals

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## Article

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# Abstract

The design and construction of photoresponsive compounds with solid-liquid transitions has been one of the central challenges in chemistry. Particularly, challenges remain for non-photoresponsive compounds. Herein, we show that a tiny dope of azobenzene (Azo) in conventional imidazolium-based ionic crystals could demonstrate light-switchable solid-liquid transitions with a rapid responsive speed. The mechanism is based on ordering structure changes of non-photoresponsive ionic crystals induced by photoisomerization of Azo. Imidazolium ionic regions facilitated Azo isomerization while Azo isomerization altered the molecular ordering of ionic crystals, with a result of solid-liquid transitions. The sharp solid-liquid transitions distinctively switched ionic conduction from insulator and conductor, applied in lightcontrolled capacitance and UV sensor. The supramolecular assembly of Azo in imidazolium-based ionic crystals provides a strategy into design of non-photoresponsive materials with photoliquefactions and successfully delivered responsiveness from molecules to macroscopic materials.

## Introduction

Solid-liquid transitions of matters are generally induced by heat. In contrast, some materials, such as azobenzene, undergo photochromic reactions that result in photoinduced isothermal solid-liquid transitions.<sup>1</sup> Azobenzene containing matters with photoinduced solid-liquid transitions have attracted intense interest because the direct phase conversions of bulk materials and the reversibility of such compounds allows reusable and resource-saving applications in various fields, such as information storage, lithography, solar energy storage, porous materials, actuators and photopharmacology.<sup>2-9</sup> However, only a few azobenzene compounds or polymers can reversibly undergo solid-liquid transitions upon light irradiations.<sup>10-14</sup>

Generally, photoisomerization of azobenzene was significantly suppressed in solid phase. Intermolecular  $\pi$ - $\pi$  stacking of azobenzene provides insufficient volume space and less flexibility to stabilize *cis*-isomers. Through complex molecular structural design, macrocyclic azobenzophane, carbohydrate conjugates, and oligoether-appended azobenzene compounds were able to display photoinduced solid-liquid transition phenomena based on successful photoisomerization of azobenzene.<sup>16-17</sup> Recently, some azobenzene polymers or compounds with light switchable glass transition temperatures or melting points were reported to demonstrate photoinduced solid-liquid transitions.<sup>13,18</sup> For example, Wu group reported that the azopolymer with methyl groups was able to demonstrate photoswitchable solid-liquid transitions while a push-pull-type azopolymer failed to induce the flow of the powders under UV illumination.<sup>18</sup> It seemed that even for azobenzene-based compounds or polymers, photoinduced solid-liquid transitions were not so easy to be obtained.<sup>19</sup> Thus, to explore diverse compounds with photoswitchable solid-liquid transitions remains a challenge, which hampers their range of applicability.

To date, little attention has been paid on liquefying non-photoresponsive materials via light with a tiny incorporation of photoresponsive compounds. This concept evolved photoliquefiable matters from molecular engineering towards supramolecular engineering. Doping azobenzene into layered liquid

crystals could demonstrate light-induced liquid crystal-isotropic liquid transitions.<sup>20</sup> We also recently reported that azobenzene molecular trigger could control sol-gel transitions of ionic liquids based on light-modulated solubility changes of thermoresponsive polymers.<sup>21–23</sup> Those methods both used fluid environments to ensure photoisomerizations, but compromised other physical properties, such as hardness. It is highly challenging to use azobenzene molecules to switch intrinsic solid-liquid transitions for non-photoresponsive compounds. A promising method to address this scientific challenge involves successful photoisomerization of azobenzene in solid state and successful photochemical effect on non-photoresponsive compounds. Until now, for non-photoresponsive compounds, no intrinsic solid-liquid transitions induced via light was reported.

Here we demonstrate a bottom-up approach to reversibly switch macroscopic solid-liquid transitions via light within seconds for non-photoresponsive imidazolium ionic crystals (ICs) by simply doping a tiny amount of azobenzene (Azo). The photo-liquefiable cores are the imidazolium crystals rather than the photoresponsive isomers, which is originated from structure ordering change in the ionic crystals altered by successful Azo isomerization. This system provides a strategy to switch ionic conductivity of the host ICs in fabricating opto-electronic devices, such as light-controlled capacitors and UV sensors. The current research opened a new avenue to achieve isothermal solid-liquid transitions for non-photoresponsive materials.

## Results

**Synthesis and characterization of Azo doped ICs.** The long alkyl chain length-based imidazolium ionic crystals ( $C_{12}VIM[X]$ ) were synthesized through anion exchange reaction with bromide precursor<sup>24</sup> and their structures were shown in Fig. 1a. Azo was mixed with six varieties of  $C_{12}VIM[X]$ , each containing an anion [X] of different size, shape, and symmetry: bromide, tetrafluoroborate, hexafluorophosphate, carbonate, thiocyanate, and perchlorate. The resulting building blocks ( $Azo-C_{12}VIM[X]$ ) are referred to hereafter as  $Azo-C_{12}VIM[Br]$ ,  $Azo-C_{12}VIM[BF_4]$ ,  $Azo-C_{12}VIM[PF_6]$ ,  $Azo-[C_{12}VIM]_2[CO_3]$ ,  $Azo-C_{12}VIM[SCN]$  and  $Azo-C_{12}VIM[ClO_4]$ , respectively.  $Azo-C_{12}VIM[X]$ , containing predominately *trans*-Azo, is defined as *trans*- $Azo-C_{12}VIM[X]$ , as opposed to *cis*- $Azo-C_{12}VIM[X]$ . The 5 wt% Azo was the optimized dose according to photoresponse and the phase compatibility of 5 wt%  $Azo-C_{12}VIM[X]$ . For neat  $C_{12}VIM[X]$ , the thermoinduced first-order solid-to-liquid transition upon heating

process was confirmed by DSC curves (Supplementary Fig. 1) and phase transition temperatures were listed in Supplementary Table 1. After an addition of Azo, crystalline structures of *trans*- $Azo-C_{12}VIM[X]$  were less altered as indicated by Power-XRD results (Supplementary Fig. 2) and mostly mixtures remained the thermoinduced solid-to-liquid transitions under POM observation (Supplementary Fig. 3). Unexpectedly, *trans*- $Azo-C_{12}VIM[Br]$  and *trans*- $Azo-C_{12}VIM[SCN]$  demonstrated a mesophase, liquid crystal phases before entering isotropic liquid state (Supplementary Figs. 4 and 5) resembled supramolecular character of Azo and ICs.

**Photoinduced solid-liquid transitions.** Photoinduced liquefaction of *trans*-Azo-C<sub>12</sub>VIM[X] was then investigated. Taken Azo-C<sub>12</sub>VIM[Br] as an example, Azo-C<sub>12</sub>VIM[Br] was illuminated by alternating 365 nm UV light and 530 nm Vis light (Fig. 1b). Under UV irradiation, the yellow powder sample of *trans*-Azo-C<sub>12</sub>VIM[Br] directly melted to give a red-orange IL within 60 s at 25°C, as shown in Fig. 1b. Also, the adjacent drops fused into single huge drops. Both indicated that UV illumination could induce flow of the *cis*-Azo-C<sub>12</sub>VIM[Br]. In contrast, Vis light irradiation frozen the fluid *cis*-Azo-C<sub>12</sub>VIM[Br] in a rather rapid speed of 50 s. By pressing the solidified *trans*-Azo-C<sub>12</sub>VIM[Br], powder cracks were observed as typical character of solids. The light switchable solid-liquid transitions were observed for non-photoresponsive C<sub>12</sub>VIM[Br] by doping a small fraction of Azo.

Additional experiments were performed to study the photoinduced solid-liquid transitions. First, the surface temperature of Azo-C<sub>12</sub>VIM[Br] under UV irradiation (180 mW/cm<sup>2</sup>) measured by an infrared thermometer, was arranged from 25 ~ 30°C (Fig. 1c), which was lower than the melting point of *trans*-Azo-C<sub>12</sub>VIM[Br] (54°C). Also, Azo-C<sub>12</sub>VIM[Br] showed a noticeable temperature discontinuity for liquefiability upon heating process. It can be liquified by UV light from 15 to 35°C, but not at a rather high temperature, such as at 38°C, no UV induced liquefaction were observed, even by prolonging UV irradiation time (Supplementary Fig. 6). In general, the photoinduced solid-liquid transitions are originated from the low melting points of the *cis*-isomers.<sup>25</sup> In such a case, the *cis*-isomers should maintain its liquid state under UV irradiation as long as the temperature is above melting points of the *cis*-isomers. Therefore, either photothermal effect or phototunable melting points of *trans*-/*cis*-isomers were insufficient to liquefy Azo-C<sub>12</sub>VIM[Br], and the solid-liquid transitions of Azo-C<sub>12</sub>VIM[Br] mainly belong to photoinduced isothermal phase transitions.

**Photoinduced ordering structure changes** Photoinduced structural changes during the solid-liquid transitions were then investigated. As shown in Fig. 2a, *trans*-Azo-C<sub>12</sub>VIM[Br] exhibited crystalline birefringence at 25°C under polarized optical microscope (POM) observations, in consistent with sharp peaks appeared in powder X-ray diffraction (XRD) patterns. The layer spacing *d* of *trans*-Azo-C<sub>12</sub>VIM[Br] was almost double for the single chain length of C<sub>12</sub>VIM[Br] based on the (001) reflection, and such double layer assembled order character is similar to the structure of the neat C<sub>12</sub>VIM[Br] compound.<sup>24,26</sup> Therefore, Azo well assembled in ICs and barely altered layer arrangements of C<sub>12</sub>VIM[Br]. Under UV irradiation, the crystalline birefringence disappeared quickly along with an absence of peaks in XRD patterns within 11 s. It suggested that UV light disturbed the ordering assembly of C<sub>12</sub>VIM[Br] with a result of the UV induced solid-to-liquid transition. Meanwhile, switching photo-irradiation from UV to Vis light caused a reversible crystallization from isotropic liquid to solid within 5 s (Supplementary Movie 1), as suggested by the reappearance of crystalline birefringence and the sharp peaks in the powder-XRD patterns in Fig. 2a. Such exceptional photoresponsive speed surpassed the previously reported solid-liquid transitions of azobenzene compounds.<sup>5,10,14</sup> Moreover, these data confirmed that the photoinduced solid-liquid transitions of Azo-C<sub>12</sub>VIM[Br] was related to photoswitchable ordering structures. It was

plausible to induce that photoresponsive order parameter determined the solid-liquid transitions for these Azo-doped ICs.

In addition, *trans*-Azo-C<sub>12</sub>VIM[Br] exhibited reversible photoinduced transitions from the liquid crystal state to the isotropic liquid state as confirmed by XRD measurements and POM observations (Supplementary Fig. 7 and Movie 2). Such liquid crystal-isotropic liquid transitions were similar to the reported azobenzene containing liquid crystal systems.<sup>20</sup>

**Photoisomerization of Azo** UV-vis absorption spectroscopy showed that Azo-C<sub>12</sub>VIM[Br] exhibited reversible photoisomerization during solid-liquid transitions (Fig. 2b). The experiments here were based on pristine photoisomerization of Azo in solid during solid-liquid transitions. Azo-C<sub>12</sub>VIM[Br] exhibited a strong  $\pi$ - $\pi^*$  band at 320 nm. Following the UV irradiation, the  $\pi$ - $\pi^*$  band of *trans*-isomers decreased and the  $n$ - $\pi^*$  band of the *cis*-isomers at 450 nm increased. The *cis*-ratio was about 53% as calculated from the intensity changes.<sup>27</sup> Subsequent visible light irradiation on *cis*-Azo-C<sub>12</sub>VIM[Br] switched it back to the *trans*-Azo-C<sub>12</sub>VIM[Br] (Fig. 2c). Those data suggested that UV induced *trans-to-cis* isomerization of Azo was able to be occurred in C<sub>12</sub>VIM[Br] crystals and under Vis light irradiation, the *cis* isomers reversed back to *trans*-isomers. Apparently, nanoscale isomerization of Azo determined macroscale solid-liquid transitions of the non-photoresponsive crystals.

It should point out that successful photoisomerization of Azo in solid phase is indispensable prerequisite for solid-liquid transitions. Photoisomerization was mostly occurred in solvent or liquid-like state, such as photoisomerization in liquid crystal mesophase.<sup>28,29</sup> Noticeably, photoisomerization of Azo here is quite different from the above, not due to liquid-like environment. In Azo-C<sub>12</sub>VIM[Br] building blocks, it was assumed that solid host C<sub>12</sub>VIM[Br] might have local free volume for the photoisomerization in microscale assembled crystalline environment.<sup>30,31</sup> Proper loosely order packed C<sub>12</sub>VIM[Br] offered enough space for successful Azo isomerization. Also, Azo and imidazolium ionic crystals has high compatibility. C<sub>12</sub>VIM[Br] might play a role of soft phase to dissolve the azobenzene phase, which might contribute to Azo isomerization in solid state.

**Ionic structure effect on photoinduced solid-liquid transitions** To study the necessary structure constituents for the photoinduced solid-liquid transitions, structure effect of cations and anions on photoresponse was then investigated. Several typical ICs with different cations have been investigated as shown in Fig. 3 and supplementary Table 2. C<sub>2</sub>VIM[Br] and C<sub>12</sub>IM[Br] are imidazolium-based cations. C<sub>12</sub>Py[Cl] and C<sub>12</sub>Amin[Br] have pyridine cations and amino cations with long alkyl chains, respectively. Both Azo-C<sub>2</sub>VIM[Br] and Azo-C<sub>12</sub>IM[Br] demonstrated UV-induced solid-to-liquid transitions under POM observations at various temperatures (Fig. 3a and b). However, Azo-C<sub>12</sub>Py[Cl] and Azo-C<sub>12</sub>Amin[Br] did not induce the flow of the powder as shown in Fig. 3c and d. UV irradiated Azo-C<sub>12</sub>Py[Cl] was further investigated by UV-vis spectra measurements and there was no *cis*-isomer appeared (Supplementary Fig. 8). It seemed that imidazolium cations are essential for photoisomerization of Azo and photoresponsive solid-liquid transitions.

By altering anions, reversible photoinduced solid-liquid transitions were observed for Azo-C<sub>12</sub>VIM[X] building blocks (Azo-C<sub>12</sub>VIM[BF<sub>4</sub>], Azo-C<sub>12</sub>VIM[PF<sub>6</sub>], Azo-[C<sub>12</sub>VIM]<sub>2</sub>[CO<sub>3</sub>], Azo-C<sub>12</sub>VIM[SCN] and Azo-C<sub>12</sub>VIM[ClO<sub>4</sub>]) at various temperatures (Supplementary Fig. 9). The liquefied temperature ranges of Azo-C<sub>12</sub>VIM[X] are depicted in Fig. 4 according to POM observations under UV and Vis light illuminations. The photoinduced solid-liquid transition temperatures were just below the melting points of the corresponding ionic crystals and greatly dependent on anions of ICs. It partially proved that ionic crystals could provide free volume space for photoisomerization of Azo. Azo-C<sub>12</sub>VIM[SCN] offered the lowest liquefied temperatures below 10°C while Azo-C<sub>12</sub>VIM[PF<sub>6</sub>] could be liquefied above 50°C. Azo-C<sub>12</sub>VIM[Br] showed the widest photoresponsive solid-liquid temperature window, ca. 20°C. Thus, the method in doping a tiny amount of Azo to achieve photoinduced solid-liquid transitions is particularly useful for non-photoresponsive imidazolium-based ICs.

**Comparison with other photoliquefiable azobenzene containing compounds** It is well-studied that azobenzene containing molecules or polymers can reversibly convert the compounds from the solids to isotropic liquids. One possible mechanism is different melting temperatures or glass transition temperatures dependent on configurations of *trans* or *cis* isomers. Wu et al reported that azobenzene-containing polymers having two quite different glass transition temperatures, facile for process fabrication.<sup>18</sup> Also, some azobenzene molecules can reversibly convert the compounds from the solids to isotropic liquids because of ordering changes. For example, by using X-ray crystal structure analysis, Hoshino et al. showed that azobenzene-containing crystal demonstrated photoinduced crystal-melt transition.<sup>11</sup>

However, the photoinduced solid-liquid transitions is different from reported ones, that is, the photoinduced solid-liquid transitions were targeted on non-photoresponsive compounds, rather than on azobenzene compounds themselves. Such photoinduced isothermal phase transitions were mostly similar with the reported azobenzene-doped liquid crystal materials, where Azo photoisomerization could induce liquid crystal-isotropic liquid transitions for the host non-photoresponsive liquid crystals.<sup>20</sup> It strongly suggest that photoinduced order changes determine the solid-liquid transitions for these Azo-doped ICs.

**Modulation of solid-liquid transitions.** Molecular dynamics simulations in a Gromacs software were conducted in order to gain insight into solid-liquid transition mechanism. Different colors for Azo were set up, at the same time, Corey-Pauling-Koltun and ball-and-stick models were used to represent azobenzene and ionic liquids, respectively to better distinguish each other. In the *trans*-Azo-C<sub>12</sub>VIM[BF<sub>4</sub>] system (Fig. 5a and 5b), the imidazolium chain distribution was more regular, while in the *cis*-Azo-C<sub>12</sub>VIM[BF<sub>4</sub>] system (Fig. 5c and 5d), the chains were distributed irregularly and the interface was curved (concave and convex). The simulation results showed that both *trans*- and *cis*-Azo were assembled around imidazolium cations and anions, which was mainly caused by van der Waals and electrostatic interaction (Supplementary Fig. 10). Upon geometric change from in-plane *trans*-Azo to out-of-plane *cis*-Azo, the ordered layer structures were perturbed with showing curved edges, ultimately resulting in an isotropic

liquid state. It seemed that photoisomerization of Azo produces intermolecular “communication” between the responsive machines and non-responsive subassemblies, thereby, phase states determined by the wholly assembled structure ordering degree amplified the nanoscale operations of Azo. FT-IR experiments were also conducted to confirm that Azo was confined nearly the ionic regions, in which UV induced vibrational changes in the imidazolium cation and in the anion (Supplementary Fig. 11). The proposed building block of Azo-C<sub>12</sub>VIM[X] not only offers a universal methodology for light-induced solid-liquid transitions of the non-photoresponsive C<sub>12</sub>VIM[X], but also makes a leap to demonstrate how Azo communicates with ionic crystals and deliver macroscale response of ICs.<sup>32</sup>

**Applications based on photoinduced solid-liquid transitions.** Due to distinguished solid-liquid transitions, ionic function could be significantly tuned by light. In crystalline state, the ions are immobilized as confined in crystalline lattices while in liquid state, the ions are flowing to demonstrate various functions of ionic liquids as illustrated in Fig. 6a. The immobilization and mobilization of ions means the switching off and on of certain ionic functions, thus more integrated functions and sophisticated opto-iontronics device of Azo-C<sub>12</sub>VIM[X] would be expected to be explored.

**Light regulated insulator-conduction transitions.** Based on the switchable solid-liquid transitions, light-controlled ionic conductivities of Azo-C<sub>12</sub>VIM[Br] were next measured by electrochemical impedance spectroscopy (EIS) to demonstrate macroscale property changes derived from nanoscale motion of molecular machines. Figure 6b shows a full frequency range of the Bode plots under Vis and UV irradiation at 15°C. For *trans*-Azo-C<sub>12</sub>VIM[Br], the impedance magnitude ( $|Z|$ ) was very high, and the phase angle ( $-\phi$ ) was close to 90°, indicating highly resistive and capacitive responses. These behaviors strongly suggest that *trans*-Azo-C<sub>12</sub>VIM[Br] behaves as an insulator as ions are frozen in the crystal lattice. Under UV irradiation,  $|Z|$  greatly decreased and  $-\phi$  approaches 0° as the frequency increased, which is typical for an ionic conductor. The

differences became more apparent when  $|Z|$  and  $-\phi$  values were compared at high frequencies (10<sup>-1</sup>-10<sup>2</sup> kHz) (Supplementary Figs. 12 and 13), indicating a UV induced sharp transition from an ionic insulator to an ionic conductor. Changes in  $|Z|$  and  $-\phi$  were repeatable (Supplementary Fig. 14 and Fig. 15). The bulk impedance ( $R_b$ ) was obtained from the Nyquist plot as shown in Fig. 6c. Upon the solid-liquid transition, *trans*- $R_b$ , 2.7 × 10<sup>8</sup> Ω, was reduced to *cis*- $R_b$ , 25 Ω, corresponding to a change in ionic conductivity  $\sigma$  from 6.1 × 10<sup>-11</sup> S/cm to 6.6 × 10<sup>-4</sup> S/cm (Fig. 6d), respectively. In short, Azo could switch ionic insulator-conductor transitions of the C<sub>12</sub>VIM[Br].

**Light-controlled capacitors.** In addition, light-controlled charge and discharge processes were demonstrated in Azo-C<sub>12</sub>VIM[Br] based electric double layer capacitors as illustrated in Fig. 6e. An Azo-C<sub>12</sub>VIM[Br] electrolyte was sandwiched by indium tin oxides (ITO) electrodes to fabricate a capacitor. Current density of the *trans*-Azo-C<sub>12</sub>VIM[Br] based capacitor was close to zero at various scan rates because of frozen ions (Fig. 6f and Supplementary Fig. 16), while a *cis*-Azo-C<sub>12</sub>VIM[Br]-based one showed stable electrochemical performance in cyclic voltammetry and galvanostatic charge-discharge tests

(Fig. 6f and Supplementary Fig. 17) with a capacitance around  $25 \mu\text{F}/\text{cm}^2$ . The rectangular-shaped CV curves (Fig. 6f) and the increasing current with an increase in the scan rates were of typical capacitance response. Thus, a light controlled capacitor concept was proposed: the capacitor could be charged in liquid state and the energy could be stored in solid state as illustrated in Fig. 6d. As shown in Fig. 6g, the open-circuit voltage ( $V_{\text{OC}}$ ) accumulated by charging *cis*-Azo- $\text{C}_{12}\text{VIM}[\text{Br}]$  was maintained at 0.23 V after immediately switching to Vis irradiation, this finding provides evidence that frozen ions can store energy. The charged state was able to be maintained by in solid *trans*-Azo- $\text{C}_{12}\text{VIM}[\text{Br}]$ . As expected, the voltage showed a rapid decline to 0 V under UV irradiation as an energy release process. Light-switched solid-to-liquid and liquid-to-solid transitions endowed charge and discharge process of the capacitors to be controlled, which might shed light on designing advanced capacitors.

**UV sensors** As an example of UV detector application, we monitored the ionic signals of Azo- $\text{C}_{12}\text{VIM}[\text{Br}]$  under various UV intensities (Fig. 6h) in a circuits with a blue LED light. By tuning various UV intensities, different ionic signals could be output with good reversibility as shown in Fig. 6h. LED light showed distinguished light intense based on various UV intensities. These findings indicate Azo- $\text{C}_{12}\text{VIM}[\text{Br}]$  with light switchable ionic resistance can output recognizable ionic signals, potentially working as a robust UV detector with rapid response. The UV sensors makes full use of each component: Azo as a molecular trigger to sense UV light, solid-liquid transitions to transfer and amplify ionic signals.

## Discussion

By physical incorporation of Azo into conventional imidazolium-based ICs, light-switchable solid-liquid transitions were demonstrated upon Azo isomerization, together with a control of ionic movability. To accomplish this solid-liquid transitions, two major problems must to be solved: successful photoisomerization of Azo in crystalline state and successful transfer of photoisomerization effect on ionic crystals. The combination of Azo and imidazolium ionic liquid just made it easy, that is, imidazolium-ionic regions provide solvent-like environments to ensure successful photoisomerization of Azo, while presence of bent *cis*-Azo disrupted layered ionic parts, with a result of solid-liquid transitions. The resulting solid-liquid transitions, enabled ionic insulator-conductor, was demonstrated to be applied in a light controlled-capacitor and UV sensor with an output of detectable and stable ionic signals. This is the first report on Azo assembled supramolecular system to demonstrate solid-liquid transitions for non-responsive compounds. The supramolecular toolbox is an attractive option to bridge stimulus molecules with functional ionic materials. Although photoliquefiable exploration for non-photoresponsive compound is only in its infancy, it provides a new perspective to explore photoresponsive materials, reusable functional materials as well as light fabrication engineering.

## Methods

Detailed procedures for the synthesis and characterization of the Azo-ICs are provided in the Supplementary Information.

## Data Availability

All data necessary to support the findings of this study are available in the Supplementary Information. The raw data are available from the corresponding author upon reasonable request. Source data are provided in this paper.

## Declarations

## Author contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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## Figures

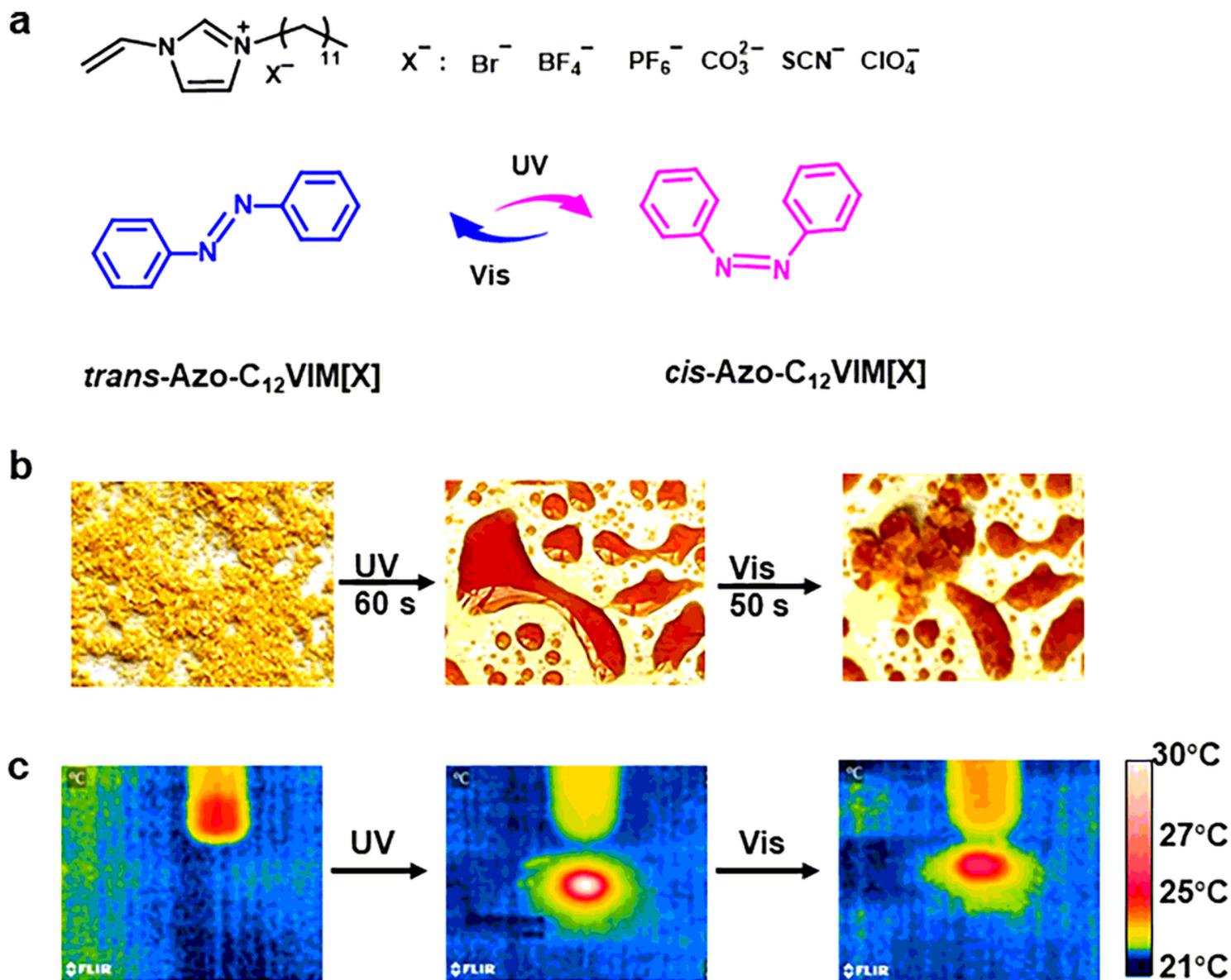


Figure 1

**Chemical structures of Azo-C<sub>12</sub>VIM[X], and photoinduced solid-liquid transitions of Azo-C<sub>12</sub>VIM[Br]. a,** Chemical structures of non-photoresponsive ICs and Azo. **b,** Optical images of Azo-C<sub>12</sub>VIM[Br] powder undergoing solid to liquid transitions under UV irradiation (365 nm, 180 mW/cm<sup>2</sup>, 60 s) and liquid-to-solid transitions under Vis light irradiation (450 nm, 100 mW/cm<sup>2</sup>, 50 s).

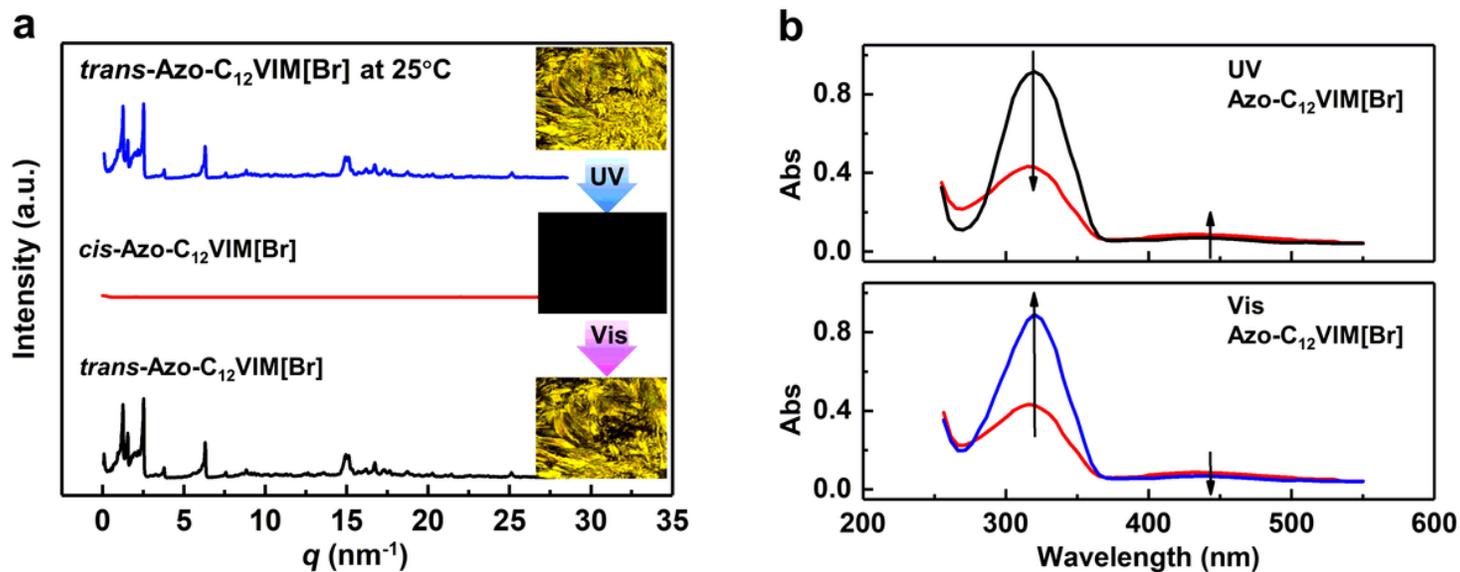


Figure 2

**Reversible ordering structure changes and photoisomerization.** a, Reversible crystal-isotropic liquid phase transitions of Azo-C<sub>12</sub>VIM[Br] detected by powder XRD at 25 °C before UV (365nm, 60 mW/cm<sup>2</sup>, 11 s) irradiation, followed by under UV and then Vis light irradiation (365nm, 10 mW/cm<sup>2</sup>, 5 s); b, UV-Vis spectra of Azo-C<sub>12</sub>VIM[Br] under UV irradiation and under Vis irradiation corresponding to solid-liquid transitions.

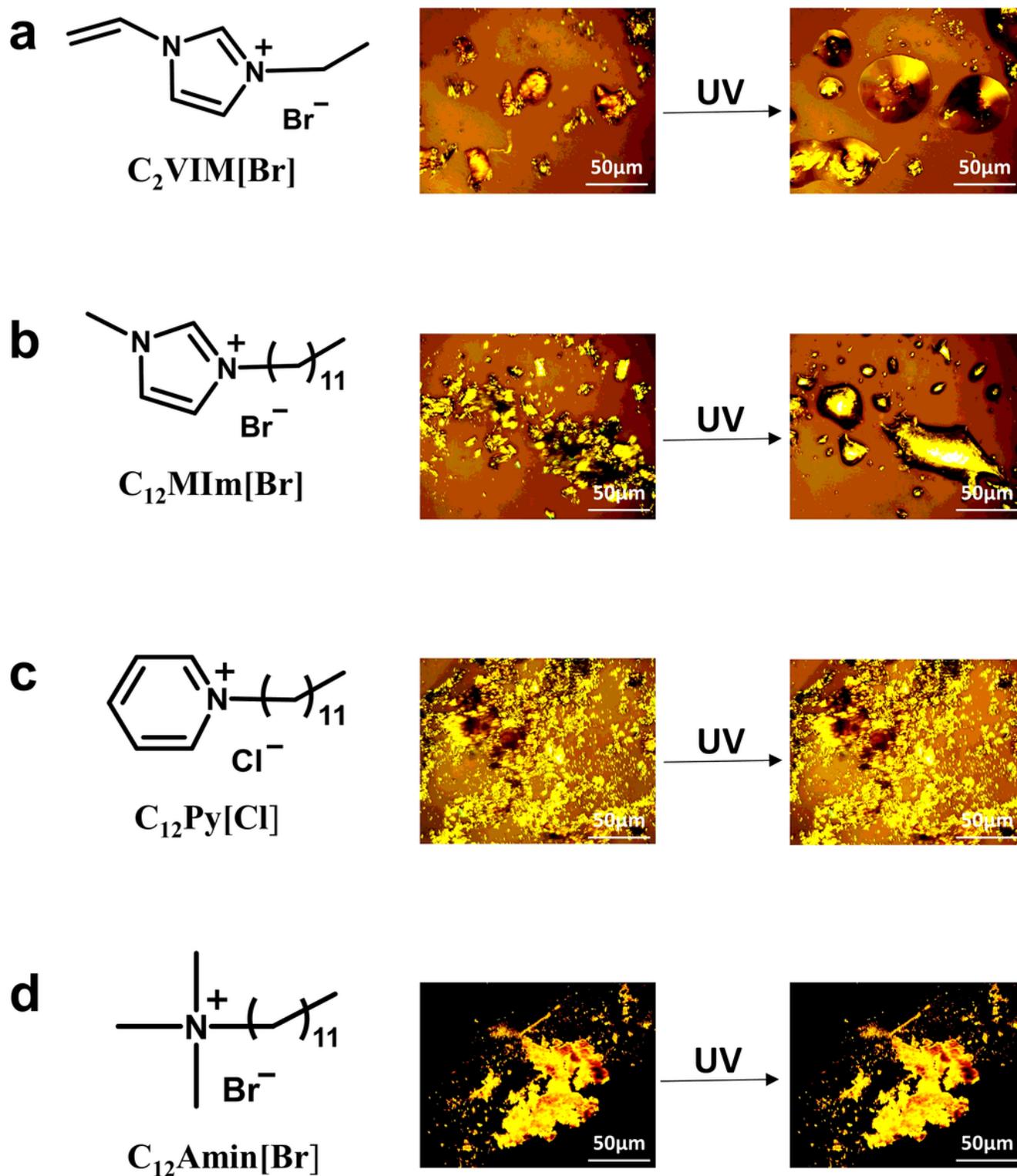


Figure 3

**Cation effect on photoresponsive solid-liquid transitions.** a-d, Optical microscopy images of powder  $C_2VIM[Br]$ (a),  $C_{12}MIm[Br]$  (b),  $C_{12}Py[Cl]$ (c) and  $C_{12}Amin[Br]$ (d) before and after 365 nm light irradiation ( $180 \text{ mW cm}^{-2}$ , 365 nm). Although UV irradiation induced the flow of  $C_2VIM[Br]$  and  $C_{12}MIm[Br]$ , it did not induce the flow of  $C_{12}Py[Cl]$  and  $C_{12}Amin[Br]$ . Scale bars, 50  $\mu\text{m}$ .

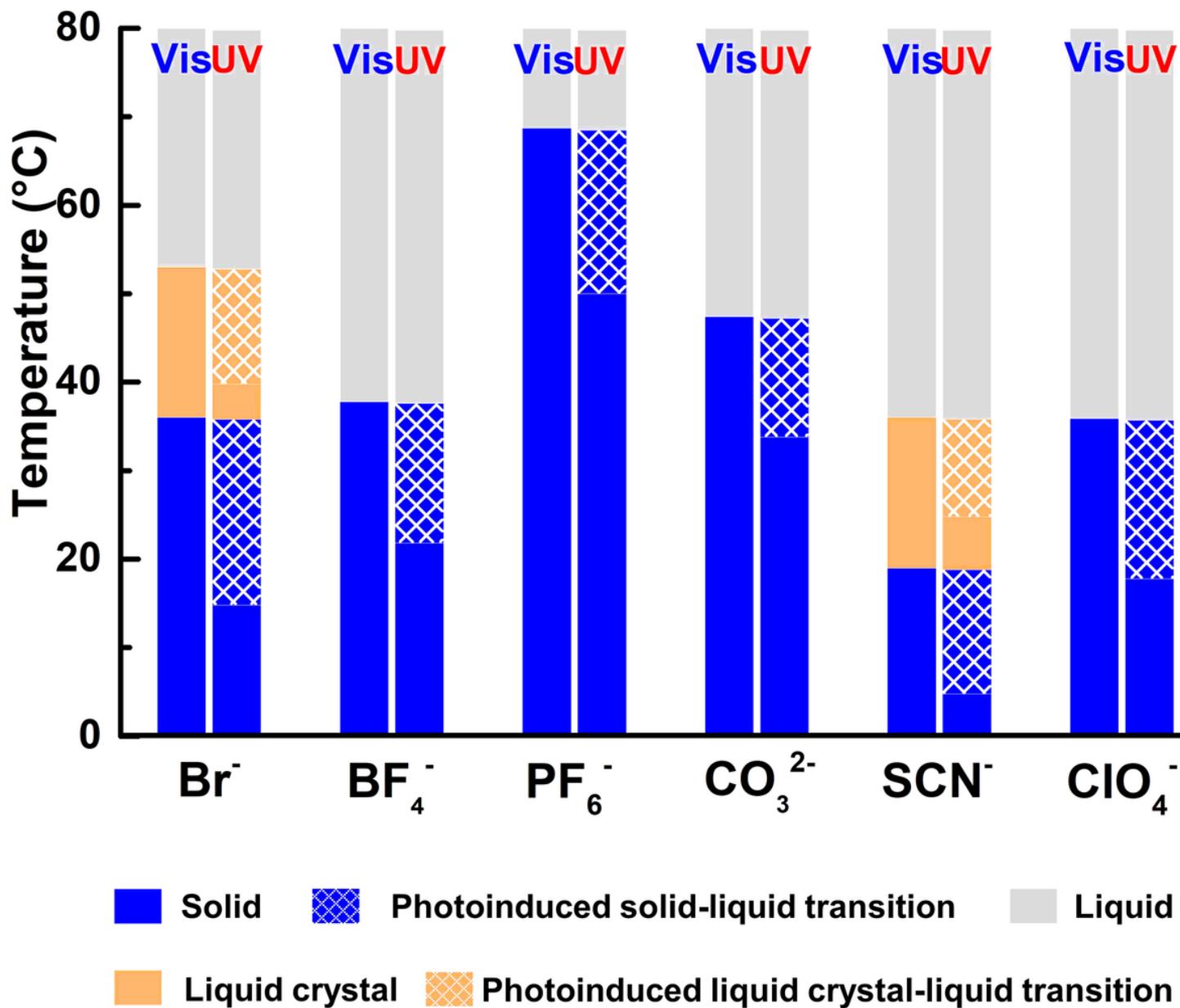
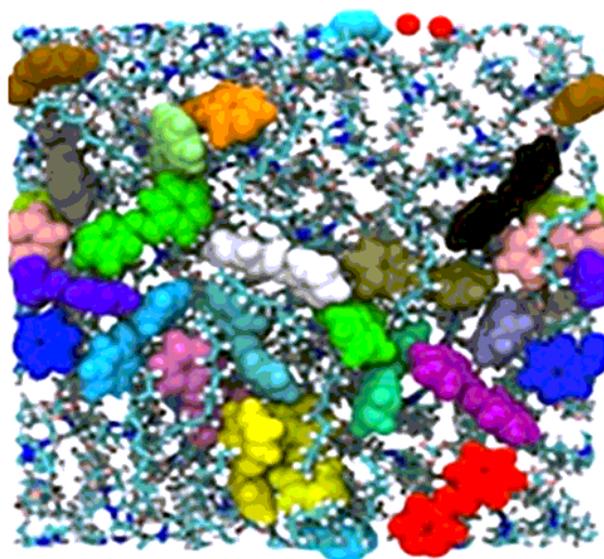
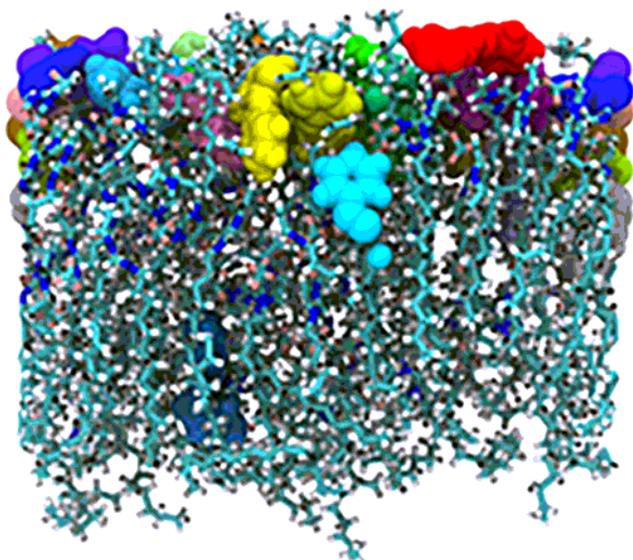


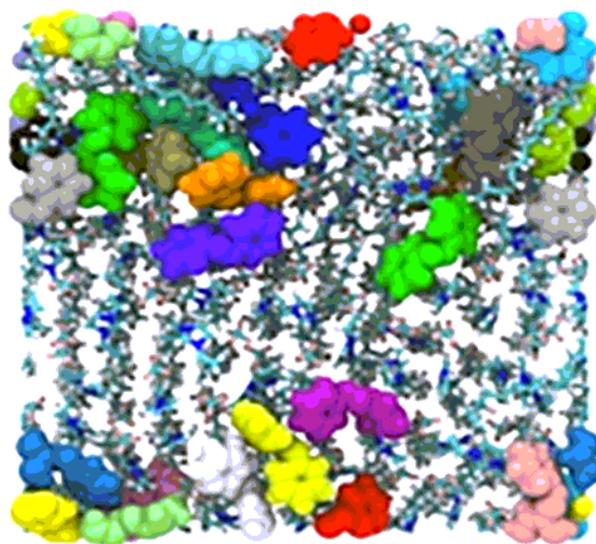
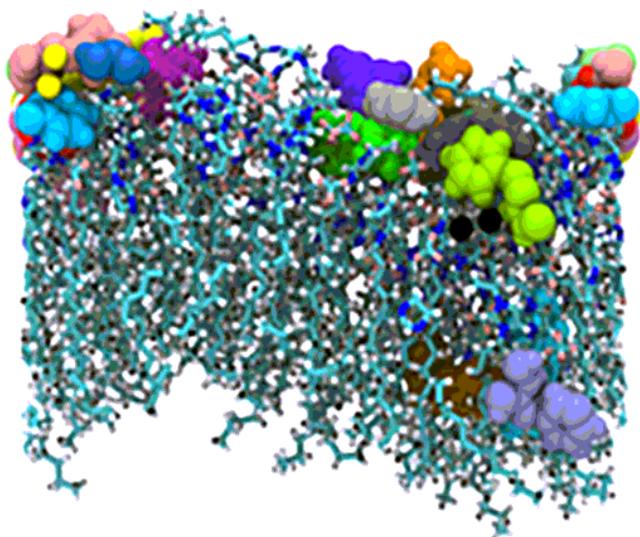
Figure 4

**Anion effect on photoresponsive solid-liquid transitions.** Photo/thermos-induced various phase transitions for Azo-C<sub>12</sub>VIM[X] compounds under UV (180 mW cm<sup>-2</sup>, 365 nm) and Vis (100 mW cm<sup>-2</sup>, 450 nm) light irradiation upon heating process under POM observation.

**a** *trans*-Azo-C<sub>12</sub>VIM[BF<sub>4</sub>]

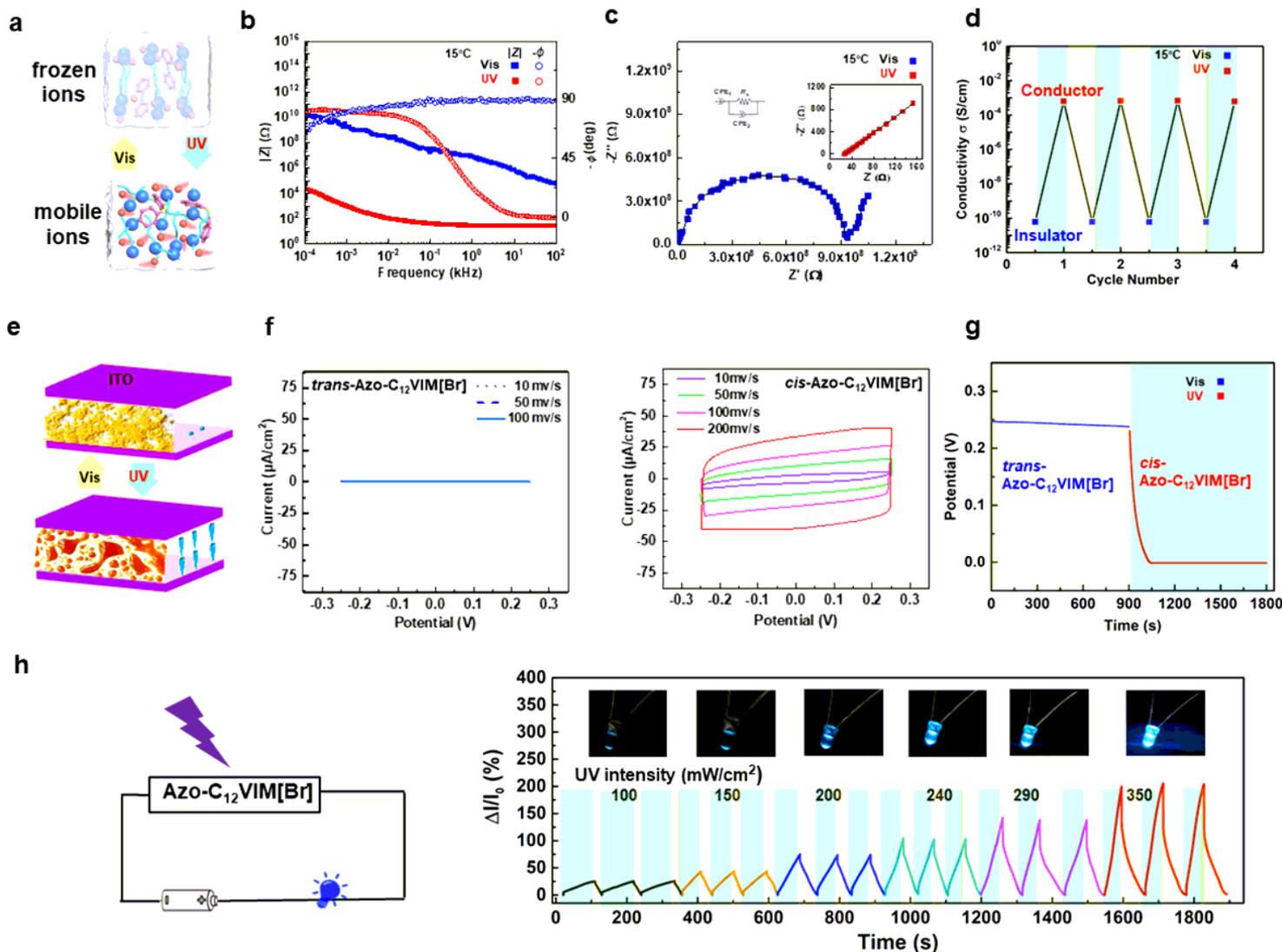


**b** *cis*-Azo-C<sub>12</sub>VIM[BF<sub>4</sub>]



**Figure 5**

**Molecular dynamics simulations of equilibrium configurations for the system.** a, Simulated arrangements of C<sub>12</sub>VIM[BF<sub>4</sub>] and *trans*-Azo calculated at 10 ns with front and vertical views; b, Simulated arrangements of C<sub>12</sub>VIM[BF<sub>4</sub>] and *cis*-Azo calculated at 10 ns with front and vertical views.



**Figure 6**

**Insulator–conductor, charge-discharge, and ionic signal output based on photoinduced solid-liquid transitions.** a, Illustration of frozen ions in crystals and mobile ions in liquids; b, Bode plots of  $|Z|$  (filled squares) and  $-\phi$  (open circles) of Azo-C<sub>12</sub>VIM[Br] at 15 °C; c, Nyquist plots of Azo-C<sub>12</sub>VIM[Br] in solid and liquid phases at 15 °C; d, Reversible insulator-conductor transitions of Azo-C<sub>12</sub>VIM[Br] at 15 °C; e, Illustration of charge-discharge processes of the Azo-C<sub>12</sub>VIM[Br]-based capacitor under UV and Vis light irradiation; f, Cyclic voltammetry curves of a *trans*-Azo-C<sub>12</sub>VIM[Br]-based capacitance and a *cis*-Azo-C<sub>12</sub>VIM[Br]-based one; g, Time dependence of open circuit voltage switched by UV and Vis light irradiation at 15 °C; h, UV sensor based on photoresponsive Azo-C<sub>12</sub>VIM[Br] at 25 °C with an output of photo-regulated ionic currents dependent on various UV intensities (100, 150, 200, 240, 290, and 350  $\text{mW}/\text{cm}^2$ ).

## Supplementary Files

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