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Phase-Tunable Fluorophores Based upon Benzobis(imidazolium) Salts

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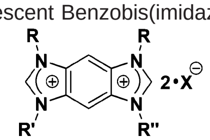
Conjugated organic salts are a versatile class of molecules that have found utilities in a multitude of applications,[1] including ion-conductive membranes for fuel cells, photovoltaics, ionic organic light-emitting diodes, and ionic liquid crystals (ILCs). One nascent area of fundamental research that may significantly advance each of these applications focuses on enhancing the photoluminescent properties of low melting organic salts (i.e., fluorescent ionic liquids (ILs)). For example, traditional imidazolium-based ILs have recently attracted attention as photoluminescent liquids.[1f−h,2,3] Unfortunately, due to their relatively small chromophores, such ILs typically display stiflingly low emission intensities in the visible region (Φ_f < 0.05), which not only complicates analytical measurements but also limits their utilities.[1f,g] To facilitate advancement in this field, we sought a means to overcome inherent barriers associated with imparting fluidic properties to rigid polycyclic aromatic systems exhibiting intense visible photoluminescence. Herein, we report a general, modular route to fluorescent, conjugated organic salts with tunable phase characteristics including ambient temperature fluidities and mesomorphic (i.e., liquid-crystalline (LC)) behavior at elevated temperatures.

Benzobis(imidazolium) (BBI) salts (see Table 1) are poised for finely tuning the phase characteristics of fluorescent conjugated organic salts. They feature (1) robust imidazolium components for dually providing phase control and high thermal stabilities, (2) fluorogenic heteroaromatic cores which should enable efficient luminescence, and (3) modular N-substituents to tailor LC phase properties. Collectively, these features should impart phase tunability as well as increased emission relative to traditional imidazolium-based ILs.

Initially, we investigated the photophysics of known BBIs **1** and **2**, which possess *N*-alkyl and *N*-aryl groups, respectively (Table 1).[4] Not only was each salt found to display a high Φ_f, their disparate λ_{max} values suggested a straightforward means to tune their electronic characteristics through N-substitution (see Table 2). Since **1** and **2** decomposed prior to melting, subsequent efforts shifted toward capitalizing on their structural features to tune phase characteristics.

Systematic structural optimization[5,6] was guided by knowledge of related ILs,[1d] as well as solid-state analysis[7] of select crystalline compounds. An advancement was made with BBI **3** which exhibited a relatively low glass transition temperature (T_g) of 89 °C due to its reduced molecular symmetry and non-coordinating counterions (cf. **1** and **2**). Building from these results, BBI **4•MeSO₄** (T_g = 43 °C) was synthesized, which takes advantage of dissimilar imidazolium rings to reduce its molecular symmetry even further. Surveying other counterions associated with the same BBI core (cf. **4•BF₄** and **4•I**) confirmed that $MeSO_4$ was ideal for lowering the T_g values of these salts.[8] By incorporating N-substituents that not only disrupted $\pi-\pi$ interactions[7] but also imparted π-facial asymmetry (**5**−**7**), a BBI with a T_g < 0 °C was ultimately synthesized. Notably, high decomposition temperatures (T_d) were observed from each of the BBIs, typically exceeding 270 °C.

Table 1. Photoluminescent Benzobis(imidazolium) Salts



BBI	R	R′	R″	X	yield[a] (%)
1	Bu	Bu	Bu	Br	93
2	Ph	Ph	Ph	Cl	48
3	Me	Ph	Ph	$MeSO_4$	86
4•MeSO₄	Me	*i*-Bu	4-BuPh	$MeSO_4$	89
4•BF₄	Me	*i*-Bu	4-BuPh	BF_4	85
4•I	Me	*i*-Bu	4-BuPh	I	88
5	Me	*i*-Bu	3-MePh	$MeSO_4$	90
6	Et	Me	3-MePh	$MeSO_4$	91
7	Et	Me	4-OctPh	$MeSO_4$	89
8a	$C_{12}H_{25}$	$C_{12}H_{25}$	$C_{12}H_{25}$	BF_4	99
8b	Me	4-OctPh	4-OctPh	BF_4	78

[a] Isolated overall yield from commercially available starting material.[5]

Table 2. Physical and Photophysical Properties of Benzobis(imidazolium) Salts

BBI	T_g[a] (°C)	T_d[b] (°C)	λ_{abs}[c] (nm)	λ_{em}[c] (nm)	Φ_f[d]
1	*e*	271 (265)	288 (4.29)	330	0.64
2	*e*	325 (314)	352 (3.94)	474	0.41
3	89	267 (263)	345 (3.31)	447	0.91
4•MeSO₄	43	273 (276)	287 (4.04)	410	0.53
4•BF₄	84	338 (335)	288 (4.27)	408	0.51
4•I	113	218 (215)	288 (4.20)	408	0.47
5	35	270 (262)	286 (4.19)	402	0.52
6	0.8	272 (269)	289 (4.01)	403	0.63
7	−0.3	274 (270)	289 (4.13)	408	0.57
8a	*f*	338 (314)	291 (4.14)	332	0.85
8b	*f*	341 (335)	348 (4.03)	451	0.72

[a] Glass transition temperature (T_g) obtained from the second heating run using DSC under N_2, rate = 5 °C/min. [b] Decomposition temperature (T_d) defined as the temperature at which 10% weight loss occurred as determined by TGA under N_2 using high-resolution analysis;[5] parenthetical values were obtained under air. [c] In MeOH under ambient conditions; log(ϵ) values in parentheses. [d] Reported quantum efficiencies (Φ_f) are relative to *E*-stilbene or anthracene. [e] No transitions observed by DSC up to the T_d. [f] Mesomorphic; see text.

As mentioned above, desirable photoluminescence properties were a key objective of our study. The absorption and emission properties of **3**−**7** were initially investigated in MeOH.[5] As summarized in Table 2, the absorption and emission spectra for **4**−**7** remained fairly consistent, which demonstrated an ability to selectively manipulate their physical properties without compromising control over electronic features. Importantly, each of the BBIs exhibited high Φ_f values (0.41−0.91), which should facilitate applications as solution-based fluorophores.

Central to our primary objective, however, was the ability of the BBI chromophore to avoid self-quenching mechanisms and

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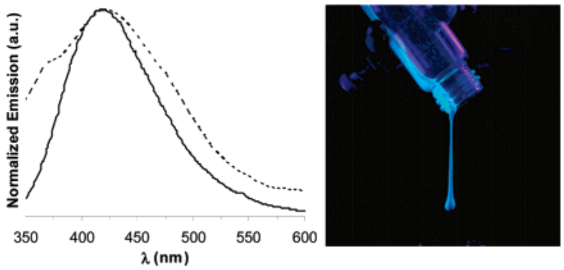

Figure 1. Left: Photoluminescence spectrum of **4•MeSO₄** in MeOH (solid line) and as a thin film (dotted line), each under ambient conditions. Right: Picture of **4•MeSO₄** heated at ca. 80 °C under irradiation from a 365 nm lamp (5 W).

Figure 2. PLM images (left: ILC **8a**, right: ILC **8b**) were obtained as LC phases and appeared upon cooling from the isotropic melt; magnification = 100×.

maintain intense emission in condensed phases. Photoluminescence was qualitatively observed from each of the glassy BBI fluorophores (i.e., **3**−**7**) at temperatures above and below their T_g value. For example, as depicted in Figure 1, bright blue emission obtained from a bulk sample of **4•MeSO₄** was found to persist at 200 °C, a temperature well above its T_g. Excitation of an annealed thin film of this material (obtained via melt-casting) produced a bright blue emission with a λ_{em} of 423 nm, consistent with the λ_{em} in solution. Collectively, these results indicated that BBI-based IL fluorophores maintained efficient luminescent properties in solution, solid state, and as flowing liquids.

Having obtained room-temperature fluorescent ILs, we shifted our focus toward fine-tuning phase control to obtain mesomorphic fluorophores based on BBIs. This was motivated largely by the observation that imparting LC behavior to neutral organic fluorophores can greatly improve their performance in electronic applications.[9] Furthermore, the BBI architecture would introduce a unique structural class of ILCs featuring rigid, polycyclic cationic cores[1i,j] similar to dye-based chromonic LCs but photoluminescent in nature.[10]

Two BBI-based mesogens, **8a** and **8b** (see Table 1), were synthesized, and each was analyzed by differential scanning calorimetry (DSC), polarized light microscopy (PLM), and variable-temperature powder X-ray diffraction (VT-PXRD).[5,11] Investigation of the DSC cooling cycles of **8a** suggested a broad LC temperature range that began at 53 °C and extended to 194 °C, at which point the material became isotropic. Upon cooling from the isotropic melt, PLM of **8a** showed an optical texture indicative of an anisotropic LC phase (Figure 2 left). VT-PXRD revealed equally spaced reflections consistent with a smectic phase.[5,12] DSC analysis of **8b** revealed a narrower but higher temperature LC range (188−238 °C). The black PLM texture of this material (Figure 2 right) and its optical transparency in the bulk under normal light were suggestive of a thermotropic cubic phase.[13] Additionally, the observation of PXRD peaks in the ratios $1/\sqrt{8}$, $1/\sqrt{9}$, $1/\sqrt{30}$, and $1/\sqrt{35}$ was consistent with **8b** adopting a bicontinuous cubic phase.[5,13] Further elaboration of the LC phases of **8a** and **8b** is underway.

In conclusion, an unprecedented series of phase-tunable fluorophores based upon highly photoluminescent BBI salts has been synthesized. A key structural feature of these fluorophores is that they incorporate imidazolium moieties, whereupon annulation leads to desirable luminescent properties. Through judicious choice of N-substituents and counterions, BBI salts with T_d values as high as 338 °C were obtained for materials that were fluidic below 0 °C. This feature also enabled access to two BBI-based mesogens, thus introducing a new platform for fluorescent ILC design. Collectively, these organic salts produced constant blue emission from solution through cooled glassy states to free flowing liquids. Considering their high thermal stabilities, amphiphilic properties, and structural modularity, BBI salts effectively form a new class of emissive chromophores with promise as processable fluorophores, sensory materials, and models for fundamental photophysical investigations.

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Supporting Information Available: Detailed experimental procedures and characterization of all new compounds are available. This material is available free of charge via the Internet at http://pubs.acs.org.

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(6) Starting from 1,5-dichloro-2,4-dinitrobenzene, BBIs **3**−**8** were synthesized in high yields via a chromatography-free S_NAr-reductive cyclization−alkylation sequence.[5] Where applicable, anion metathesis from the corresponding BBI diiodide was performed according to literature protocol; see: Vu, P. D.; Boydston, A. J.; Bielawski, C. W. *Green Chem.* **2007**, *9*, 1158.
(7) X-ray crystallographic analysis of **3** revealed infinite rows of dimers which were attributed to $\pi-\pi$ facial interactions between the polycyclic cores of the molecules. In contrast, solid-state analysis of **6** confirmed that $\pi-\pi$ interactions had been disrupted.[5]
(8) Notably, the dicationic BBIs can accommodate two dissimilar counterions. For example, incorporating one BF_4 and one $MeSO_4$ anion (i.e., mixing equimolar amounts of **4•MeSO₄** and **4•BF₄**, or anion metathesis[6] of **4•I** with 1.0 molar equiv each of Me_3O•BF_4 and Me_2SO_4) produced a BBI with a T_g of 19 °C.
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(11) The solution absorption and photoluminescence of compounds **8a** and **8b** were consistent with their structural analogues **1** and **3**, respectively (see Table 2).
(12) The smectic LC phase layer spacing was found to be less than the molecular length, indicating some tail interdigitation and/or molecular tilt in the layers. Similarly, the single-crystal structure of **8a** showed a layered arrangement with overlapping alkyl chains.[5]
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