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## Anion-induced ionic liquid crystals of diphenylviologens †

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Two series of ionic liquid crystals derived from diphenylviologens **1-2** were prepared and their photophysical and electrochemical properties were also investigated. Crystallographic data of two single crystals **1-RSO**<sub>3</sub> (n = 10) and **2-BF**<sub>4</sub> (n = 12) showed that a mono– or bilayer–lamellar structure was induced by intermolecular H–bonds. All mesophases were identified as smectic A phases by POM textures and powder XRD data. A linear correlation plot ( $R^2 = 0.8885$ ) of the *d*–spacings with the calculated effective radius ( $R_{eff}$ ) in compounds **2-X** was obtained. Aggregation–induced emission (AIE) ranged from ca. 463–529 nm observed in compounds **2-X** (*e.g.*, X = BF<sub>4</sub>, PF<sub>6</sub>, RSO<sub>3</sub>, OTf and NTf<sub>2</sub>) was also anions dependent. Also these compounds **2-X** exhibited thermal switch with On/Off–emission mode between Cr and SmA phases. On cyclic voltammograms, compound **1-RSO**<sub>3</sub> (n = 12) formed spike–like voltammetric peak potentials without redox couples.

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<sup>†</sup>Electronic supplementary information (ESI) available: the <sup>1</sup>H, <sup>13</sup>C and <sup>19</sup>F NMR spectra of

compounds 1-2, the DSC and TGA thermographs of compounds 2-NTf<sub>2</sub>, 2-BF<sub>4</sub> and 2-SCN, the XRD diffraction plots of compounds 2-BF<sub>4</sub> and 2-SCN, the UV-Vis and PLspectra of compounds 2-NTf<sub>2</sub>, and he cyclic voltammograms of compounds 1-RSO<sub>3</sub> and 2-RSO<sub>3</sub>

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## I. Introduction

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Ionic liquid crystals (ILCs) which can effectively merge the characteristic of liquid crystals (LCs) with those of ionic liquids (ILs) have entirely distinct properties from those of conventional organic molecular compounds. Although Knight and Shaw had reported the first pyridinium-based ILCs<sup>1</sup> since 1938, this field of interest has been revived again during the last two decades. A few extensive reviews<sup>2-4</sup> for these ILCs were reported. Original researches described about pyridinium-based ILCs were mostly focused on the halide salts.<sup>1, 5-11</sup> The mesophases observed were mostly smectic A phases, in which an ionic bilayer structure sandwiched by the anions between the pyridinium ring was proposed.<sup>5, 8, 11,12</sup> Other counter ions were further reported.<sup>12-18</sup> The study of the influence of the anion has been developed in other series of ionic liquid crystals.<sup>19-22</sup> For association to ionic bilayer mesogens of pyridinium salts, a few series of N,N'-disubstituted-4,4'-bipyridinium salts (viologens) were investigated.<sup>23-41</sup> The ionic interactions inherent, same as pyridinium-based ILCs tended to stabilize lamellar mesophases, e.g., SmA,<sup>23-27, 30, 34-36</sup> SmB,<sup>31</sup> SmC<sup>41</sup> and SmX.<sup>35, 39, 41</sup> However, they also displayed other mesophases such as cubics,<sup>40</sup> columnar phases<sup>29, 33, 37</sup> or lamellar columns.<sup>36,40</sup> Among the viologen-based mesogens reported (Fig. 1), most of them were those structures containing N-alky chains, but not N-aryl substituted on the pyridine. This structural limitation might be due their complicated synthesis. The importance of about H-bonds in ionic liquids<sup>42</sup> has been reviewed by P. A. Hunt. The ionic mesogens induced through H-bond interactions in pyridinium-based ILCs has also been described.<sup>12</sup>

Moreover, the merit in thermochromic,<sup>43</sup> photochromic<sup>44</sup> or/and electrochromic<sup>45</sup> properties of the viologens has recently attracting significant attention. These technologies have been potential candidates for applications in various fields, such as single–molecule transistors,<sup>46</sup> LCDs,<sup>47</sup> smart windows or antiglare car mirrors,<sup>48-49</sup> OLEDs,<sup>50</sup> charge storage<sup>51</sup> and sensors.<sup>52</sup> In the field of luminescent liquid crystals, the aggregation–caused quenching (ACQ) effect is common to most luminophores, and the  $\pi$ – $\pi$  stacking interactions existent between well packing molecules were attributed or/and prompted to the formation of excimers, leading to the observed ACQ effect.

Another photophysical phenomenon in sharp contrast to the ACQ effect is aggregation<sup>O</sup> induced<sup>BTCO3090A</sup> emission (AIE). An AIE process associated with possible mechanisms, such as restriction of intramolecular motion (RIM), J–aggregate formation (JAF), twisted intramolecular charge transfer (TICT) and excited–state intramolecular proton transfer (ESIPT) has been summarized by B. Z. Tang.<sup>53</sup> Based on the RIM process, viologen–based ILCs which were not luminescent or weak in solution but exhibited strong fluorescence in aggregation or solid state might provide the possibility to fabricate novel AIE–active ILCs by introducing peripheral counter ion or flexible alkyl chains to the viologen cores.



Fig. 1 Known examples of viologen-based mesogens with N-alkyl chain substitution.

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In this work, instead of using a soft long N–alkyl chain, ionic mesogens with a rigid–core of N–phenylpyridinium chlorides prepared via Zincke reactions<sup>54</sup> were reported. Among them, two types of ionic structures were constructed. One series of diphenylviologen **1-RSO**<sub>3</sub> has alkyl chains incorporated as counter anion while the other series are di(alkoxy)phenylviologens **2-X** with a variety of counter anions incorporated; **X**<sup>–</sup> = bis(trifluoromethane)sulfonylimide (NTf<sub>2</sub><sup>–</sup>), alkylsulfonate (RSO<sub>3</sub><sup>–)</sup>, triflate (OTf<sup>–</sup>), tetrafluoroborate (BF<sub>4</sub><sup>–</sup>), hexafluorophosphate (PF<sub>6</sub><sup>–</sup>) and thiocyanate (SCN<sup>–</sup>). **Fig. 2** shows the molecular structures of ionic mesogens with rigid–core of diphenylviologens **1** and di(4–alkoxyphenyl)viologens **2**. In order to understand the steric hindrance, correlation of the alkyl chain length and/or the counter anion on the formation of the mesophases in such types of ionic bipyridinium–based ILCs, a systematic study on a total number of 13 ionic

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view Article Online compounds was prepared and investigated. The mesomorphic properties of these ionic Compounds<sup>03090A</sup> were studied by use of POM, DSC, TGA and XRD.



Fig. 2 The molecular structures of diphenylviologens 1-RSO<sub>3</sub> and di(4–alkoxyphenyl)viologens2-X.

The crystallographic data obtained from two representative crystals **1-RSO**<sub>3</sub> (n = 10) and **2-BF**<sub>4</sub> (n = 12) established the crystal structures and molecular structures in this type of ILCs. Powder XRD data also supported the proposed model of the anions sandwiched between the bipyridinium rings.<sup>5, 8, 11, 18</sup> XRD data indicated that a monolayer and a bilayer lamellar structure in the crystal lattices was formed for di(4-alkoxyphenyl)viologens **2** and diphenylviologens **1**, respectively. There continues to be a growing interest in recent developments<sup>44, 55-59</sup> for AIE–active viologen derivatives. Both photophysical and electrochemical properties of the rigid–core of viologens **1-2** were also studied.

#### **II. Results and discussion**

#### Synthesis and characterization

The synthetic pathways to compounds **1-2** are listed in **Scheme 1**. The precursors of diphenyl viologen dichloride **1-Cl** and di(4-alkoxyphenyl)viologen dichlorides **2-Cl** ( $\mathbf{R} = \mathbf{C}_n \mathbf{H}_{2n+1}$ , n = 10, 12, 14) via Zincke reactions followed by the methods in the literature<sup>60-61</sup> were obtained. These viologen–based precursors were identified by <sup>1</sup>H–NMR and <sup>19</sup>F–NMR spectroscopy. For example,  $\delta$  7.80–7.82 (m, 6H) and 8.01 (dd, 4H, J = 7.5, 1.5 Hz) were assigned to the Ph–H and  $\delta$  9.15 (d, 4H, J = 6.6 Hz), 9.75 (d, 4H, J = 6.6 Hz) were assigned to the Py–H for diphenyl viologen dichloride **1-Cl**.

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Similarly, two characteristic peaks at  $\delta$  7.30 (d, 4H, J = 9.0 Hz) and 7.86 (d, 4H,  $J = 8.9^{1}$  Hz) 3% effective of the second assigned to the Ph–H and the other peaks at  $\delta$  8.88 (br, 4H) and 9.49 (br, 4H) were assigned to the Pv–H for di(4–alkoxyphenyl)viologen dichloride 2-Cl) Then methanol used as a phase–transfer medium was added in the metathesis of counter anions. The soft counter anion salt solution, for example sodium alkylsulfonate (RSO<sub>3</sub>Na), sodium tetrafluoroborate (NaBF<sub>4</sub>), potassium hexafluorophosphate (KPF<sub>6</sub>), lithium triflate (LiOTf), lithium bis(trifluoromethane)sulfonimide (LiNT $f_2$ ) or potassium thiocyanate (KSCN) dissolved in water was added to their precursors **1-Cl** or **2-Cl** dissolved in methanol/dichloromethane (CH<sub>3</sub>OH/CH<sub>2</sub>Cl<sub>2</sub> = 1/5). The reaction was continuously stirred at 35–40 °C for 3 h. This ion–exchange reaction was monitored using an alumina TLC plate with an eluent of CH<sub>3</sub>OH/CH<sub>2</sub>Cl<sub>2</sub> (5/95) in which the retention factor ( $R_f \sim 0.6$ ) of the product was higher than the  $R_f \sim 0.1$  of the precursor. The organic layer was passed through a short alumina (Al<sub>2</sub>O<sub>3</sub>) flash column. The products were obtained after recrystallization from isopropanol/ethyl acetate mixture. The <sup>13</sup>C–NMR spectra of compounds 2-X were not obtained due to their poor solubility in common solvents. The <sup>1</sup>H- or <sup>19</sup>F-nuclear magnetic resonance spectroscopy (NMR) was used to identify their structures, for example, on <sup>1</sup>H–NMR spectra, all the PyH–peaks for bipyridinium – based derivatives 1-X and 2-X were easily differentiated with their precursors 1-Cl and 2-Cl. The individual peak integration of bipyridinium and alkylsulfonate for either 1-RSO3 or 2-RSO<sub>3</sub> was equivalently obtained, confirming the stoichiometric coefficient for each moiety of the ion pair. On <sup>19</sup>F–NMR spectra, for example, the characteristic peaks appeared at  $\delta = -153.57$  and -153.62 (s, BF<sub>4</sub><sup>-</sup>), -74.4 (d, J = 707 Hz, PF<sub>6</sub><sup>-</sup>), -79.6 (s, OTf<sup>-</sup>) and -80.2 (s, NTf<sub>2</sub><sup>-</sup>) identified and confirmed all of the fluorine-containing compounds. Positive (or negative) ion moieties were recorded using the electrospray ionization-high resolution mass spectrometry (ESI-HRMS) to confirm the target structures.

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Scheme 1. Reagents and conditions: (i) Stirred in CH<sub>3</sub>CN, 80 °C, 24 h, 97%; (ii) Aniline, stirred in DMAc, 90-95 °C, 14 h, 87%; (iii) 4-Alkoxyphenylamine, stirred in DMAc, 90-95 °C, 24 h, 74%; (iv) Aqueous RSO<sub>3</sub>Na, methanol/CH<sub>2</sub>Cl<sub>2</sub> (1/5), 35-40 °C, 3 h, 95%; (v) Aqueous NaBF<sub>4</sub>, KPF<sub>6</sub>, RSO<sub>3</sub>Na, LiNTf<sub>2</sub> LiOTf NaBF<sub>4</sub>, KPF<sub>6</sub>, KSCN stirred in CH<sub>3</sub>OH/CH<sub>2</sub>Cl<sub>2</sub> (1/5), 35-40 °C, 3 h, 95%.

Single crystal and molecular structures of N,N'-diphenyl-4,4'-bipyridinium di(decylsulfonate) 1-RSO<sub>3</sub> (n = 10) and N,N'-bis(4-dodecoxyphenyl)-4,4'-bipyridinium di(tetrafluoroborate) 2-BF<sub>4</sub> (n = 12).

In order to understand the correlation between the ionic molecular structures and mesomorphic behavior of these two types of ionic mesogens, two single crystals of the mesogenic compounds **1-RSO3** (n = 10) and **2-BF4** (n = 12) suitable for crystallographic analysis were obtained by slow vaporization from mixed solvent of isopropanol/ethyl acetate at room temperature and their structures resolved. Fig. 3 shows two molecular structures with the atomic numbering schemes. Table 1 lists their crystallographic and structural refinement data for the two crystals. They all crystallize in a triclinic space group P-1 with a Z = 1 and Z = 2, respectively.

	<b>1-RSO3</b> $(n = 10)$	<b>2-BF</b> <sub>4</sub> $(n = 12)$
Empirical formula	$C_{42} \ H_{68} \ N_2 \ O_{10} \ S_2$	$C_{46}H_{67}B_2F_8N_2O_{2.50}$
Formula weight (g mol <sup>-1</sup> )	825.10	861.63
Temperature (K)	200(2)	200(2)
Wavelength (Å)	1.54178	1.54178
Crystal system	Triclinic	Triclinic
Space group	<i>P</i> -1	<i>P</i> -1
a (Å)	6.2986(10)	7.7273(2)
b (Å)	9.3042(2)	10.0812(3)
c (Å)	18.9025(4)	30.1503(9)
α (°)	83.2337(7)	98.0699(10)
β (°)	85.7251(71)	93.6023(11)
γ (°)	86.4000(8)	93.0372(11)
Volume (Å <sup>3</sup> )	1095.34(4)	2316.32(11)
Z	1	2
Density (calculated) (Mg/m <sup>3</sup> )	1.251	1.235
Crystal size (mm <sup>3</sup> )	0.253x0.115x0.085	0.353x0.223x0.026
$\theta$ range for data collection (°)	2.359 to 69.996	2.968 to 69.985
Data/restraints/parameters	4147/6/291	8748/16/572
Final R1, wR2	R1 = 0.0395,	R1 = 0.0692,
	wR2 = 0.1063	wR2 = 0.1827

Table 1 Crystallographic and refinement details for compounds 1-RSO3 and 2-BF4. DOI: 10.1039/C8TC03090A

The overall molecular shapes of two crystals were considered as linear shapes, and the molecular lengths were ca. 36.62 Å (atom C21–C21 in **1-RSO**<sub>3</sub>) and 47.64 Å (atom C23–C23 in **2-BF**<sub>4</sub>). Both bipyridine–rings in crystals **1-RSO**<sub>3</sub> and **2-BF**<sub>4</sub> were nearly coplanar, leading to a small dihedral angle of 1.1° and 0.4°. The small dihedral angles obtained were quite different from twisted bipyridine rings of other dialkylviologens.<sup>38</sup> A relatively large dihedral angle of ca. 32.5–47.0° between pyridine and phenyl ring in these diphenylbipyrindiniums was observed. Two counter ions (decyl)SO<sub>3</sub><sup>-</sup> and BF<sub>4</sub><sup>-</sup> in both crystals were orderly intercalated between the bipyridinium layers. Interestingly, two hydrated water molecules were cooperated in crystal lattice **1-RSO**<sub>3</sub>.

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Fig. 3 Two ORTEP plots of 1-RSO<sub>3</sub> (n = 10, top) and 2-BF<sub>4</sub> (n = 12, bottom) with the atomic numbering schemes, thermal ellipsoids are shown at the 50% level. Hydrogens were omitted for clarity.

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In the crystal lattices, intermolecular H–bonds and Coulombic forces between cations and anions were found to be more dominant. Indeed, H–bonds with a weak to medium strength were observed, for example, H–bonds (C–H...O) of bipyridinium–H and sulfonate–O anion or hydrated water in crystal **1-RSO**<sub>3</sub> (n = 10), H–bonds C–H...F of bipyridinium–H and borate–F in crystal **2-BF**<sub>4</sub> (n = 12) were all observed. These H–bond lengths ranged approximately from  $d = 1.947 \sim 2.507$  Å (in **1-RSO**<sub>3</sub>), from  $d = 2.286 \sim 2.591$  Å (in **2-BF**<sub>4</sub>, **Fig. 4**). The formation of H–bonds was responsible for a better or preferred packing both in the solid or/and the liquid crystal states. Some H–bonds observed between the cations and anions in these two crystals are listed in **Table 2**.



Fig. 4 H-bonds (red dash line) connected around the bipyridinium with counter anions observed in crystals **1-RSO<sub>3</sub>** (n = 10, left plot) and **2-BF**<sub>4</sub> (n = 12, right plot).

Compd.	No. of H-bonds	Bond distance/Å	Bond angle/ <sup>o</sup>
1-RSO <sub>3</sub>	2	O3H4A = 1.947	$\angle$ S1-O3-H4A = 122.8
	2	H5BO4 = 1.987	$\angle$ O5-H5B-O4 = 170.4
	2	H4O5 = 2.027	$\angle$ C4-H4-O5 = 163.8
	2	O1H4B = 2.137	$\angle$ S1-O1-H4B = 103.8
	2	H1O2 = 2.263	$\angle C1 - H1 - O2 = 162.9$
	2	H7O5 = 2.310	$\angle$ C7–H7–O5 = 138.6
	2	H2O5 = 2.400	$\angle$ C2-H2-O5 = 171.0
	2	H8O2 = 2.450	$\angle$ C8-H8-O2 = 151.3
	2	H11O1 = 2.507	∠ C11–H11–O1 = 171.0
2-BF4	2	H1F8 = 2.286	$\angle C1 - H1 - F8 = 169.4$
	2	H11F1 = 2.487	$\angle$ C11-H11-F1 = 152.4
	2	H7F2 = 2.509	$\angle$ C7-H7-F2 = 120.8
	2	H5F7 = 2.522	$\angle$ C5-H5-F7 = 126.9
	2	H1F6 = 2.584	$\angle C1 - H1 - F6 = 124.7$
	2	H5F5 = 2.591	$\angle C5-H5-F5 = 144.2$

Table 2 Intermolecular H-bonds observed in crystal 1-RSO3 and 2-BF4.

On the other hand, Coulombic forces and intermolecular  $\pi - \pi$  interactions in these ILCs were also critical in these lattices, as shown in Fig. 5. Considering the formal charge between the more positive  $N^{\delta+}$  atoms and nearby standing negative  $F^{\delta-}$  (or  $O^{\delta-}$ ) atoms, the crystal packing model was mainly

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driven by the Coulombic interactions. Crystallographic data indicated that the distance of the <sup>9/CBTC03090A</sup> Coulombic force when packed with sulfonate anion was approximately d = 3.991-4.042 Å in **1-RSO**<sub>3</sub>, which was weaker than those in **2-BF4**, d = 2.882-2.922 Å. Furthermore, weak intermolecular  $\pi-\pi$  interactions between the neighboring diphenylbipyridiniums were also observed in crystals **1-RSO**<sub>3</sub>. A  $\pi-\pi$  distance ranged at d = 3.680-3.756 Å was obtained in **1-RSO**<sub>3</sub>. However, a distance of d = 7.727 Å showed no intermolecular  $\pi-\pi$  interactions in **2-BF4** due to the intercalated counter anions. The Coulombic forces (d = 3.991-4.042 Å) were much weaker than the H–bonds (d= 1.947–2.507 Å) in **1-RSO**<sub>3</sub>, whereas the Coulombic forces (d = 2.882-2.922 Å) were just slightly weaker than the H–bonds (d = 2.286-2.591 Å) in **2-BF4**. In contrast, the intermolecular  $\pi-\pi$ interactions (d = 3.680-3.756 Å) were slightly stronger than the Coulombic forces (d = 3.991-4.042Å) in **1-RSO**<sub>3</sub>.



Fig. 5 Coulombic forces (red dash line) and intermolecular interactions (blue dash line) observed in 1-RSO<sub>3</sub> (n = 10, left) and 2-BF<sub>4</sub> (n = 12, right) in the crystal lattices.

All the terminal alkyl chains were interdigitated between layers by a style of layer–by–layer and head–to–tail arrangements (see **Fig. 6**). The lamellar bilayer structures in compounds **1-RSO**<sub>3</sub> were formed in a head–to–head arrangement with sulfonate–head groups in apposition. Bipyridiniums were aligned in a line–by–line style; the counter alkylsulfonate anions were similarly intercalated or linked (**Fig. 6**). However, monolayered lamellar structures in compounds **2-BF**<sub>4</sub> were formed by an

end-to-end style in which the counter  $BF_4^-$  was in fact sandwiched between the cationic bipyridinium rings (**Fig. 6**). The bipyridiniums in compound **1-RSO**<sub>3</sub> inclined at the lamellar level, but the di(alkoxyphenyl)bipydiniums in compounds **2** stood at the upright direction.



**Fig. 6** Crystal packing viewed down a–axis. Interdigitated bilayers in diphenylviologen **1-RSO**<sub>3</sub> (n = 10, left plot) and interdigitated monolayers in di(dodecoxyphenyl)viologen **2-BF**<sub>4</sub> (n = 12, right plot).

#### Mesomorphic properties and thermal stability

The thermal behavior of compounds **1-RSO**<sub>3</sub> and **2-X** (X = RSO<sub>3</sub>, NTf<sub>2</sub>, OTf, BF<sub>4</sub>, PF<sub>6</sub> and SCN) was investigated using polarized optical microscopy (POM) and differential scanning calorimetry (DSC). The transition temperatures and enthalpies of the compounds **2** are listed in **Table 3**. All these viologens **1-2** exhibited mesogenic behavior, which was expected for rod–like molecules. On cooling from the isotropic liquid phase, smectic A phase with a focal–conic texture or homeotropic texture was common observed (**Fig. 7**). These SmA phases were also confirmed as bilayer structures for **1-RSO**<sub>3</sub> or monolayer structures for **2-X** by using powder X–ray diffraction experiments (see discussion later). For the series of viologen **1-RSO**<sub>3</sub>, the melting temperature remained at  $T_{mp} = 88.7-113.1$  °C, whereas the clearing temperature ( $T_{cl}$ ) increased with carbon length, *i.e.*,  $T_{cl} = 217$  (n = 10) < 256 (n = 12) < 275 °C (n = 14). The temperature range of SmA phases increased with carbon

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length,  $\Delta T_{\text{SmA}} = 118.5$  (n = 10) < 196.3 (n = 12) < 223.0 °C (n = 14) on cooling.

For the series of viologens 2-X, all compounds exhibited SmA phases. However, the clearing temperature was quite sensitive to the anions incorporated;  $T_{cl} = 337.0$  (2-OTf) > 336.0 (2-BF4) > 312.0 (2-PF<sub>6</sub>) > 304.8 (2-NTf<sub>2</sub>) > 274.0 (2-SCN) > 220.2 °C (2-RSO<sub>3</sub>) for the n = 12 derivative. This decreasing in clearing temperature was not quite correlated with effective radius of the anions (discussed later). Not surprisingly, compound 2-RSO<sub>3</sub> substituted with both alkyl-chains at cation and anion moieties exhibited higher melting temperatures by  $\Delta T_{mp} = 31.7$  (n = 10) < 43.8 (n = 12) < 50.0 °C (n = 14) and lower clearing temperatures  $\Delta T_{cl} = 0.3$  (n = 10) < 35.8 (n = 12) < 71.3 °C (n = 14) than those of compounds 1-RSO<sub>3</sub>. This change in both clearing and melting temperature led to a smaller temperature range of SmA phase, i.e.  $\Delta T_{\text{SmA}} = 92.4$  (n = 10) – 86.0 °C (n = 14) which might be attributed to the much more hydrophobic interaction than Coulumbic and H–bond interactions. Similarly, for the series of viologens 2-NTf<sub>2</sub>, the melting temperature remained at 103.8–104.5 °C, but the clearing temperature ( $T_{cl}$ ) increased with carbon length, *i.e.*,  $T_{cl} = 254.3$  (n = 10) < 304.8 (n = 10) 12) < 328.0 °C (n = 14). The temperature range of SmA phase increased with carbon length, i.e.  $\Delta T_{\text{SmA}} = 156.3 \ (n = 10) < 203.3 \ (n = 12) < 228.8 \ ^{\circ}\text{C} \ (n = 14) \text{ on cooling. The dependence of the}$ mesogenic behavior was often observed in melting and clearing temperature increase with elongation of alkyl chain.<sup>7</sup>



**Fig. 7** Optical textures observed: (a) SmA phase by **1-RSO**<sub>3</sub> (n = 10) cooling at 210 °C; (b) SmA phase by **2-NTf**<sub>2</sub> (n = 10) at 247 °C; (c) SmA phase by **2-RSO**<sub>3</sub> (n = 10) at 205 °C.

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Table 3. The transition temperatures<sup>a</sup> and enthalpies of compounds 1-2

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1-RSO <sub>3</sub> ; n = 10		Cr	<u>112.0 (3.35)</u> 96.5 (0.74)	SmA	217.0 <sup>b</sup> 215.0 <sup>b</sup>	I
12		Cr	<u>113.1 (3.50)</u> 57.7 (5.83)	SmA	256.0 <sup>b</sup>	I
14		Cr	88.7 (0.93) 46.0 (16.2)	SmA	275.0 <sup>b</sup>	I <sub>d</sub>
2-RSO <sub>3</sub> ; n = 10		Cr	<u>143.7 (31.4)</u> 120.3 (26.0)	SmA	216.7 (1.81) 212.7 (1.74)	I
12		Cr	<u>156.9 (25.5)</u> 132.7 (22.0)	SmA	220.2 (1.08)	I
14		Cr	<u>138.7 (40.7)</u> 101.3 (35.1)	SmA	203.7 (2.22) 187.3 (0.64)	I
2-NTf <sub>2</sub> ; n = 10		Cr	<u>104.3 (43.5)</u> 97.3 (37.2)	SmA	<u>254.3 (2.22)</u> 253.6 (2.24)	I
12		Cr	<u>104.5 (56.8)</u> 94.5 (51.2)	SmA	<u>304.8 (3.41)</u> 297.8 (2.09)	I
14		Cr	<u>103.8 (53.7)</u> 95.2 (53.5)	SmA	328.0 <sup>b</sup> 324.0 <sup>b</sup>	I
2-PF <sub>6</sub> ; n = 12		Cr	<u>162.0 (40.4)</u> 143.2 (42.7)	SmA	312.0	dec.
2-SCN; n = 12	$Cr_1 \xrightarrow{108.5 (34.5)}_{73.4 (72.8)} Cr_2 \xrightarrow{118.1 (51.7)}_{80.6 (1.25)}$	<mark>∍</mark> SmX	<u>153.9 (2.39)</u> 146.1 (2.33)	SmA	274.0	dec.
2-BF <sub>4</sub> ; n = 12	$Cr_1 = \frac{107.8 (64.8)}{85.7 (41.9)} Cr_2 = \frac{140.4 (2.98)}{121.2 (1.24)}$	- SmX	<u>153.8 (1.22)</u> 144.4 (1.69)	SmA	336.0	dec.
2-OTf; n = 12		Cr	<u>131.7 (27.4)</u> 99.4 (11.0)	SmA	337.0	dec.

<sup>a</sup>: n is the carbon numbers of the terminal alkoxy chains. Cr = crystal, SmA = smectic phase, I = isotropic, dec = decomposed. All data were determined by DSC at a scan rate of 10 <sup>0</sup>C/min.

<sup>b</sup>: observed by POM.

In order to understand the effect of counter anions incorporated in such type of mesogenic diviologen **2-X**, six compounds with different anions (X = BF<sub>4</sub>, PF<sub>6</sub>, OTf, NTf<sub>2</sub>, RSO<sub>3</sub>, SCN) were prepared and their mesomorphic behavior was compared. Surprisingly, all compounds **2-X** were mesogenic regardless of the type of counter anions, as shown in **Fig. 8**. These bipyridinium–based mesogens showed a higher  $T_{cl}$  and wider  $\Delta T_{SmA}$  than those of pyridinium–based mesogens in the literatures.<sup>12</sup> Four ionic salts with small anionic moiety (X = BF<sub>4</sub>, PF<sub>6</sub>, OTf, SCN) resulted in decomposition before clearing point. An extra more ordered SmX phase for compounds **2-BF<sub>4</sub>** or **2-SCN** were observed which was also confirmed by powder XRD (see discussion later). Interestingly, a new volume–based approach predicting thermophysical behavior of ionic liquids

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and ionic liquid crystals was reported by Nelyubina.<sup>62</sup>

Fig. 8 Bar graphs showing the thermal mesomorphism of compounds 2-X (for all n = 12).

The thermal stability of compounds 2-X (n = 12) was also performed by thermogravimetric analyses (TGA) under nitrogen atmosphere, shown in **Fig. 9**. Different counter anion showed different thermal stabilities. All six compounds showed good thermal stability at a temperature below ca. 270 °C. The decomposition temperatures were obtained for a 5% weight loss. The relative stability of these compounds 2-X followed by a  $T_{dec} = 344.0$  (2-NTf<sub>2</sub>) > 337.2 (2-OTf) > 336.5 (2-BF4) > 312.5 (2-PF6) > 299.5 (2-RSO<sub>3</sub>) > 274.5 °C (2-SCN).



Fig. 9 The TGA thermograms of compounds 2-X.

### **Powder X-ray diffractions**

Variable temperature powder X-ray diffraction experiments were performed to confirm the structure of the SmA phases for compounds 1-2. All the samples (except 2-BF4, 2-PF6, 2-SCN) were first heated above their  $T_{\rm cl}$ , then cooled down to a mesophase temperature and the diffraction data were collected. The X-ray diffraction data are summarized in **Table 4**. All compounds 1-2 were rod-shaped molecules, and they exhibited SmA phases. In most cases, all XRD patterns showed a typical lamellar diffraction pattern of layered structures in which one strong peak and one very weak peak at small angle region and also a broad halo peak at large angle were observed. These two diffraction peaks at lower angle were assigned as index 001 and 002, which were typically characteristics of layer structures observed for a SmA phase. For example, for compounds 1-RSO<sub>3</sub> (n = 12) at 180.0 °C a diffraction pattern with one strong peak at 27.1 Å and one very weak peak at 13.6 Å at small angle region was observed (Fig. 10). The lamellar thickness of 27.1 Å for compound **1-RSO<sub>3</sub>** (n = 12) with a bilayer structure was slightly shorter than that of compound **2-RSO<sub>3</sub>** at 30.8 Å with a monolayer structure. Other compounds 2-X exhibited similar diffraction patterns of SmA phase as compound **1-RSO**<sub>3</sub>. However, the layer distance or thickness for the compounds **2-X** in SmA phase was sensitive to the compounds;  $d = 38.9 (2-SCN) > 36.2 (2-BF_4) > 35.6 (2-PF_6) > 34.8$  $(2-OTf) > 30.8 (2-RSO_3) > 30.5 \text{ Å} (2-NTf_2)$ . Additional two peaks at 13.0 and 9.8 Å for compound 2-SCN assigned as indices 003, 004, and one peak at 11.7 Å for compound 2-OTf assigned as 003 were also observed. Furthermore, two compounds 2-BF4 and 2-SCN also showed a SmX phase at lower temperature at 140 and 150 °C, respectively.

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Fig. 10 The powder X–ray diffraction plots by compound 1-RSO<sub>3</sub> (n = 12, top) at 180 °C, compound 2-RSO<sub>3</sub> (n = 12, middle) at 210 °C and compound 2-NTf<sub>2</sub> (n = 12, bottom) at 180 °C.

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Compds	Mesophase temp.	d–Spacing(Å) obs. (calcd.)	Miller indices
1–RSO3 <sup>a</sup>	SmA at 180 °C	27.1 (27.1) 13.6 (13.6) 5.0 (br)	001 002 halo
2–SCN <sup>b</sup>	SmX at 140 °C	39.9 (39.9) 19.9 (20.0) 13.3 (13.3) 9.9 (10.0) 4.7 (br) 4.2 (br)	001 002 003 004 halo halo
	SmA at 160 °C	38.9 (38.9) 19.4 (19.5) 13.0 (13.0) 9.8 (9.7) 4.2 (br)	001 002 003 004 halo
<b>2–BF</b> 4 <sup>b</sup>	SmX at 150 °C	36.0 (36.0) 18.1 (18.0) 4.7 (br)	001 001 halo
	SmA at 160 °C	36.2 (36.2) 18.2 (18.1) 4.8 (br)	001 002 halo
2–PF6 <sup>b</sup>	SmA at 260 °C	35.6 (35.6) 17.9 (17.8) 4.7 (br)	001 002 halo
2–OTf <sup>a</sup>	SmA at 210 °C	34.8 (34.8) 17.5 (17.4) 11.7 (11.6) 4.8 (br)	001 002 003 halo
2–RSO <sup>3<sup>a</sup></sup>	SmA at 210 °C	30.8 (30.8) 15.5 (15.4) 5.0 (br)	001 002 halo
2–NTf <sub>2</sub> <sup>a</sup>	SmA at 180 °C	30.5 (30.5) 5.0 (br)	001 halo

**Table 4** Detailed indexation by powder XRD for compound **1-2** (all n = 12)

<sup>a</sup>: temperature taken on the cooling process.

<sup>b</sup>: temperature taken on the heating process.

The dependence of *d*-spacing in the layered SmA phase with the carbon lengths was also performed. The plots of lamellar thickness with various carbon length for **1-RSO<sub>3</sub>** ( $R^2 = 0.9954$ ), **2-RSO<sub>3</sub>** ( $R^2 = 0.9409$ ) and **2-NTf<sub>2</sub>** ( $R^2 = 0.9995$ ) were shown in **Fig. 11**. For example, all XRD data showed a good 34

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correlation of the *d*-spacing with the carbon length, for example, i.e. d = 24.7 (n = 10)  $\approx 127.3^{\circ}$  ( $n = 1220^{\circ}$   $\approx 29.5$  Å (n = 14) in compounds **1-RSO**<sub>3</sub>. The other two series of compounds **2-RSO**<sub>3</sub> and **2-NTf**<sub>2</sub> showed a similar trend of *d*-spacing with carbon length.



**Fig. 11** The correlation of *d*-spacing of Lamellar thickness with carbon length in **1-RSO**<sub>3</sub>, **2-RSO**<sub>3</sub> and **2-NTf**<sub>2</sub>.

Another interesting feature was observed on the effect of *d*–spacing with counter anions in compounds **2-X**. The effective ionic radii are calculated assuming that the studied ions have a spherical shape by the equation of  $V = (4/3)\pi R^3$ . The molecular volume (V) of various anions were provided to calculate the effective radii ( $R_{eff}$ ) of anions: [SCN]<sup>-</sup> = 1.93 Å,<sup>63</sup> [BF<sub>4</sub>]<sup>-</sup> = 2.05 Å,<sup>64</sup> [PF<sub>6</sub>]<sup>-</sup> = 2.59 Å,<sup>65</sup> [TfO]<sup>-</sup> = 2.75 Å<sup>65</sup> and [Tf<sub>2</sub>N]<sup>-</sup> = 3.72 Å.<sup>66</sup> The results appeared that the *d*–spacing decreased with increasing ion radius (**Fig. 12**, R<sup>2</sup> = 0.8885). Those results showed negatively correlated with the XRD data obtained; larger *d*–spacing for smaller anions (*i.e.*, SCN<sup>-</sup>) and smaller *d*–spacing for large anions (*i.e.* TfO<sup>-</sup>, Tf<sub>2</sub>N<sup>-</sup> and RSO<sub>3</sub><sup>-</sup>). The broad halo peaks also showed an positive correlation; *i.e. d* = 4.2 Å (smaller SCN<sup>-</sup>) < *d* = 4.7–4.8 Å (medium anion, BF<sub>4</sub><sup>-</sup>, PF<sub>6</sub><sup>-</sup>, OTf<sup>-</sup>) < *d* = 5.0 Å (larger anion, NTf<sub>2</sub><sup>-</sup> or RSO<sub>3</sub><sup>-</sup>). The degree of alkoxy interdigitation might be attributed to the change in the lamellar distance; the more interdigitating for large counter anions, the shorter

#### *d*-spacing it exhibited.

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**Fig. 12** The dependence of the *d*-spacing with the effective radius of counter anions in compounds **2-X**.

#### Photophysical and electrochemical properties

Photophysical characteristics for all viologens 1-2 (all n = 12) are listed in **Table 5**. The absorption  $\lambda_{\text{max}}$  peak of diphenylviologen 1-RSO<sub>3</sub> in methanol at 314 nm is attributed to  $\pi - \pi^*$  transition. Di(4-alkoxyphenyl)viologens 2-RSO<sub>3</sub> exhibits a red–shift by  $\Delta\lambda_{\text{max}} = 68.2$  nm due to the incorporation of two more electron–donating alkoxy chains (**Fig. 13**). All  $\lambda_{\text{max}}$  for compounds 2-X were not sensitive to the counter anions, and they were all ranged in  $\lambda_{\text{max}} = 378.6-385.0$  nm due to their similar core structures. Interestingly, the absorption  $\lambda_{\text{max}}$  peaks for these viologens 1 or 2 in methanol at 314 nm or 379–385 nm are shorter than those in dichloromethane at 320 nm or 396–407 nm. These negative solvatochromism corresponded to hypsochromic shift (or blue shift) with increasing solvent polarity. All methanol solutions of viologens 1-2 were detected without any observable signals on photoluminescence. But the 2-RSO<sub>3</sub> will aggregate in the aqueous mixture with high water fractions ( $f_w$ ) needed to turn on their light emission process. As shown in Fig. 14, weak PL signals are recorded at  $f_w < 50\%$  because the luminogens 2-RSO<sub>3</sub> and 2-NTf<sub>2</sub> are fully dissolved and quenched in these solvent compositions. The PL intensity started to enhance at  $f_w > 50\%$  till it reached to the maximum intensity at  $f_w \sim 70\%$ . Normally, these viologen–based

luminogens except 1-RSO3 and 2-SCN emitted variable lights at the maximum wavelength of C8TC03090A

463–529 nm from sky–blue to yellow. The quantum yields were ranged in 0.014–0.097 (**Fig. 13** & **Table 5**). Surprisingly, the representative solid–film of viologen **2-NTf**<sub>2</sub> exhibited an on–off mode for photoluminescence when excited at 522 nm (on–mode) in crystal phase and quenched (off–mode) in SmA phase (**Fig. 15**). The flexible alkyl chains enhanced the non–radioactive relaxation while melting at SmA phase.

Compds	Abs <sub>max</sub> <sup>a</sup> /nm	Abs <sub>max</sub> <sup>b</sup> /nm	AIE max $c,d/(\Phi/nm)$
compus			
<b>1-RSO</b> <sub>3</sub>	314.0	320.0	n.d.
<b>2-RSO</b> <sub>3</sub>	382.2	395.5	529.0 (0.078)
<b>2-BF</b> <sub>4</sub>	384.4	399.0	523.5 (0.014)
2-PF6	380.4	402.0	463.0 (0.078)
2-OTf	382.8	400.5	478.7 (0.068)
<b>2-NTf</b> <sub>2</sub>	385.0	406.5	508.1 (0.097)
2-SCN	378.6	400.5	n.d.

**Table 5** Summary of photophysical data for compounds 1-2 (all n = 12).

<sup>a</sup>: The solution (10 ppm) in methanol was measured at room temperature.

<sup>b</sup>: The solution (10 ppm) in CH<sub>2</sub>Cl<sub>2</sub> was measured at room temperature.

<sup>c</sup>: Quantum yield was calculated with anthracene in ethanol ( $\Phi = 0.27$ ) as the standard.

<sup>d</sup>: The suspended mixture (20  $\mu$ M in 70%  $f_w$  water/methanol) was measured at room temperature.

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**Fig. 13** (a) UV absorption of compounds **1-2** in MeOH (solid lines) & CH<sub>2</sub>Cl<sub>2</sub> (dash lines); (b) fluorescence spectra and photographic aggregation images for compounds **1-2** in 70%  $f_w$  water/methanol mixtures (The insert graphs were taken under UV illumination).

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**Fig.14** (a) Photoluminescence spectra of compound **2-RSO**<sub>3</sub> (n = 12; left plot) in methanol and water/methanol mixtures (concentration ~ 20 µM); (b) Plots of the emission intensities *v.s.* water fractions ( $f_w$ ) for **2-RSO**<sub>3</sub> (n = 12, right plot) & **2-NTf**<sub>2</sub> (n = 12, right plot) in methanol and water/methanol mixtures (concentration ~ 20 µM). PL Spectra were excited at 525 and 505 nm for **2-RSO**<sub>3</sub> and **2-NTf**<sub>2</sub>.



**Fig. 15** Photoluminescence spectra (red–line in Cr phase and blue–line in SmA phase) and the two photographs of **2-NTf<sub>2</sub>**. The test chip was measured by Konica Minolta CS–1000S spectro radiometer under 365 nm UV light irradiation and the inserted graphs were taken under UV illumination.

The electrochemical redox reactions of viologens (**Scheme 2**) were often followed by  $D^{2}$  two<sup>039/C8TC03090A</sup> sequential one–electron–transfer reactions; from divalent cation (Vio<sup>2+</sup>) to form firstly a radical cation (Vio<sup>+</sup>) and secondly a neutral bipyridinylidene (Vio<sup>0</sup>). The  $E_1$  and  $E_2$  values were obtained from the potential of the first and second redox process.



Scheme 2 Electrochemical redox reactions in viologens.

For the voltammetric measurements, use of the half wave potential  $E = (E_p^{(\text{anodic})} + E_p^{(\text{cathodic})})/2$  can be compared to the value  $E^{\text{Fc}}$  of the ferrocene/ferrocenium as the internal standard to determine the relative potential.<sup>67-68</sup> **Fig. 16a** presents typical cyclic voltammograms with reversible couples for the first redox process (Vio<sup>2+</sup>/Vio<sup>+</sup>) of viologens **1-RSO**<sub>3</sub> and **2-RSO**<sub>3</sub> at varying sweep rates from 0.025 to 1 V/s. Peaks separation increased with increasing scan rate. Good linear tendencies (R<sup>2</sup> = 0.9953, 0.9937) of anodic peak current on square root of sweep rate for their reductions (Vio<sup>2+</sup>/Vio<sup>+</sup>) observed at **Fig. 16b** indeed well met the Rendles–Sevcik equation;  $I_p = 0.4463$  $F^{3/2}R^{-1/2}n^{3/2}c_0AD^{1/2}v^{1/2}$ , where is the sweep rate and *v* is the sweep rate.

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**Fig. 16** Cyclic voltammetry for compounds**1-RSO**<sub>3</sub> and **2-RSO**<sub>3</sub> at varying sweep rates (top plots); dependence of anodic peak current on square root of sweep rate for their reductions ( $Vio^{2+}/Vio^{+}$ ) (bottom plot).

Moreover, the viologen **1-RSO**<sub>3</sub> (n = 12) exhibits two distinct, reversible redox couples on cyclic voltammogram, and its half wave potentials  $E_1 = -0.718$  and  $E_2 = -0.970$  V (vs  $E^{Fc}$ ) measured in DMSO (**Fig. 17**) were similar to those performed in DMF.<sup>69</sup> The viologen **2-RSO**<sub>3</sub> containing long chains exhibited  $E_1 = -0.727$ V (vs  $E^{Fc}$ ) and spike–like voltammetric peak potentials ( $E_P^{c-1} = -0.055$  and  $E_P^{a-2} = -0.315$  V; vs Ag/AgCl) without redox couples on its cyclic voltammogram. This behavior has been concluded<sup>70-72</sup> that the spike response originates from potential–driven phase transition associated with reduction of the long chain containing viologen. It leaded to form a 2D

condensed film (**Fig. 18**) on the graphite cathode surface, was different to that non–alky12thatk<sup>C8TC03090A</sup> containing viologen formed gas–like adsorption layer. The results of bulk materials above may develop new prospects for redox–active (or electrochromic) liquid crystals.



**Fig. 17** Voltammograms of viologens: (a) two reversible redox couples of **1-RSO**<sub>3</sub> (left) and (b) spike–like peaks of **2-RSO**<sub>3</sub> (right).



Fig. 18 Different behaviors of viologens 1(left) and 2 (right) exhibited on an electrode surface.

## **III. Experimental**

### General materials and methods

All chemicals and solvents were reagent grade from Alfa Aesar, Sigma Aldrich or Acros chemical Co. and used as received.

NMR analysis: <sup>1</sup>H–NMR (300 MHz), <sup>13</sup>C–NMR (75 MHz) and <sup>19</sup>F–NMR (282 MHz) spectra were <sup>3090A</sup> recorded on Bruker DRS–300.

Elemental analyses: Elemental analyses were made on Elementar vario EL III.

ESI-MS analysis: Mass spectra of positive (or negative) ion moiety were recorded on JEOL

JMS-700 by electrospray ionization method.

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DSC analysis: Differential scanning calorimetry (DSC) measurements were performed on samples of about 3mg. Phase transitions were measured on Mettler DSC–822 and calibrated with a pure indium sample. All phase transitions were determined by a scan rate of 10.0 °C/min. The heating and cooling rates were 10°C/min.

TGA analysis: All measurements were performed on samples of about 4.0 mg determined on Mettler SDTA 851 by a scan rate of 20.0 °C/min.

Thermo–optical polarizing microscopy: Zeiss Axioplan 2 polarising microscope was used; equipped with a Mettler FP90/FP82HT hot stage. Pictures were taken using a digital Zeiss AxioCam MRC4 camera with a resolution of 4 megapixels in combination with Zeiss AxioVision software.

PXRD: The powder diffraction data were collected from the Wiggler–A beam line of the National Synchrotron Radiation Research Center (NSRRC) with a wavelength of 1.3223Å. The powder samples were charged in Lindemann capillary tubes (80 mm long and 0.01mm thick) purchased from Charles Supper Co. with an inner diameter of 1.0 mm,

UV–Vis spectrometry: Hitachi U3300 UV–Vis. spectrometer was used and all measurements were performed on 10 ppm various sample solution at room temperature.

Photoluminescence spectrometry: All measurements using Horiba FluoroMax–3 were performed on various samples of 20  $\mu$ M solution or suspension while excited by the appointed wave length. Cyclic voltammetry: All measurements were performed on various samples with 0.05M tertabutylammonium–BF<sub>4</sub> of DMSO solution. The solution filled in the cell with Ag/AgCl reference electrode, Pt auxiliary electrode and Graphite working electrode was carried out under N<sub>2</sub> gas atmosphere to obtain the voltammogram.

Synthesis of N,N'-bis(2,4-dinitrophenyl)-4,4'-bipyridinium dichloride<sup>60</sup> **3.** 4,4'-Bipyridine (2.0 g, 12.8 mmol) and 2,4-dinitrochlorobenzene (8.6 g, 42.4 mmol) were dissolved in acetonitrile (25 mL). The initially clear reaction mixture became gradually muddy and the solution was then stirred at 80 °C for 24 h. Solid was collected through filtration. The product isolated as white powder was obtained after washing with warm acetonitrile and desiccating in a vacuum oven. Yield 97%; <sup>1</sup>H–NMR (300 MHz, CD<sub>3</sub>OD):  $\delta$  8.43 (d, 2H, Ph–H, *J* = 8.7 Hz), 8.99 (dd, 2H, Ph–H, *J* = 2.4, 8.7 Hz), 9.11 (d, 4H, Py–H, *J* = 6.0 Hz),  $\delta$  9.34 (d, 2H, Ph–H, *J* = 2.1 Hz), 9.67 (d, 4H, Py–H, *J* = 5.7 Hz).

Synthesis of N,N'-diphenyl-4,4'-bipyridinium dichloride<sup>60</sup> 1-Cl. The mixture of freshly distilled aniline (0.78 g, 8.4 mmol) and N,N'-bis(2,4-dinitrophenyl)-4,4'-bipyridinium dichloride **3** (2.25 g, 4 mmol) were slowly added N,N-dimethylacetamide (40 mL). The solution was stirred at 90–95 °C for 14 h. Ethyl acetate (40 mL) was then added dropwise below 60 °C. Crude product was collected. The products isolated as white powder were obtained after recrystallization from methanol. Yield 87%; <sup>1</sup>H–NMR (300 MHz, DMSO–d<sub>6</sub>): 7.80–7.82 (m, 6H, Ph–H), 8.01 (dd, 4H, Ph–H, *J* = 7.5, 1.5 Hz), 9.15 (d, 4H, Py–H, *J* = 6.6 Hz), 9.75 (d, 4H, Py–H, *J* = 6.6 Hz).

General synthetic procedures of N,N'-diphenyl-4,4'-bipyridinium di(dodecylsulfonate) 1-RSO<sub>3</sub> (n = 12). To the suspension of sodium 1-dodecanesulfonate (300 mg, 1.1 mmol) in pure water (5.0 mL), 1-Cl (191 mg, 0.5 mmol) in methanol/CH<sub>2</sub>Cl<sub>2</sub> (1/5, 30 mL) was added. This reaction was monitored using TLC (Al<sub>2</sub>O<sub>3</sub>) with CH<sub>3</sub>OH/CH<sub>2</sub>Cl<sub>2</sub> (5/95) as eluent and the R<sub>f</sub> ~ 0.6 of the product was higher than the R<sub>f</sub> ~ 0.1 of 1-Cl. The organic layer was passed through a short Al<sub>2</sub>O<sub>3</sub> flash column. The crude product was obtained after solvents removed. The products 1-RSO<sub>3</sub> isolated as off–white powder were obtained after recrystallization from isopropanol/ethyl acetate in an ice–bath. Yield 95%; <sup>1</sup>H–NMR (300 MHz, CDCl<sub>3</sub>): 0.86 (t, 6H, –CH<sub>3</sub>, J = 6.9 Hz), 1.19–1.31 (m, 36H, –CH<sub>2</sub>), 1.56–1.64 (m, 4H, –CH<sub>2</sub>), 2.57–2.62 (m, 4H, –SO<sub>2</sub>CH<sub>2</sub>), 7.58 (m, 6H, Ph–H), 7.85 (m, 4H, Ph–H), 9.19 (d, 4H, Py–H, J = 6.0 Hz), 9.36 (d, 4H, Py–H, J = 6.0 Hz). <sup>13</sup>C–NMR (75 MHz, CDCl<sub>3</sub>): 14.24,

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/iew Article Online 22.82, 25.41, 29.11, 29.49, 29.58, 29.70, 29.79, 32.05, 52.21, 124.34, 128.94, 131.02, P32.09, P2.40, 0A 145.59, 150.18. ESI-HRMS (+ve): m/z calcd for C<sub>22</sub>H<sub>18</sub>N<sub>2</sub>: 155.0730 [M<sup>2+</sup>/2z]; found: 155.0726. ESI-HRMS (-ve): *m*/*z* calcd for C<sub>12</sub>H<sub>25</sub>O<sub>3</sub>S: 249.1530 [M<sup>-</sup>]; found: 249.1517. Anal. calcd for C<sub>46</sub>H<sub>68</sub>N<sub>2</sub>O<sub>6</sub>S<sub>2</sub>•4H<sub>2</sub>O: C, 62.70; H, 8.69; N, 3.18; S, 7.28; found: C, 62.48; H, 8.78; N, 3.16; S, 6.99. N,N'-Diphenyl-4,4'-bipyridinium di(decylsulfonate) 1-RSO<sub>3</sub> (*n* = 10). Off-white powder; <sup>1</sup>H–NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  0.85 (t, 6H, –CH<sub>3</sub>, J = 6.9 Hz), 1.17–1.26 (m, 28H, –CH<sub>2</sub>), 1.54–1.61 (m, 4H, –CH<sub>2</sub>), 2.54–2.60 (m, 4H, –SO<sub>2</sub>CH<sub>2</sub>), 7.57 (m, 6H, Ph–H), 7.85 (m, 4H, Ph–H), 9.17 (d, 4H, Py–H, J = 6.3 Hz), 9.37 (d, 4H, Py–H, J = 6.3 Hz). <sup>13</sup>C–NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$ 14.24, 22.79, 25.28, 29.04, 29.45, 29.54, 29.70, 32.01, 52.02, 124.39, 128.53, 130.83, 131.80, 142.42, 145.58, 150.01. ESI-HRMS (+ve): m/z calcd for C<sub>22</sub>H<sub>18</sub>N<sub>2</sub>: 155.0730 [M<sup>2+</sup>/2z]; found: 155.0726. ESI-HRMS (-ve): m/z calcd for C<sub>10</sub>H<sub>21</sub>O<sub>3</sub>S: 221.1217 [M<sup>-</sup>]; found: 221.1208. Anal. calcd for C<sub>42</sub>H<sub>60</sub>N<sub>2</sub>O<sub>6</sub>S<sub>2</sub>•3H<sub>2</sub>O: C, 62.50; H, 8.24; N, 3.47; S, 7.95; found: C, 62.45; H, 8.41; N, 3.38; S, 7.85. N,N'-Diphenyl-4,4'-bipyridinium di(tetradecylsulfonate) 1-RSO<sub>3</sub> (*n* = 14). Off–white powder; <sup>1</sup>H–NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  0.86 (t, 6H, –CH<sub>3</sub>, J = 6.9 Hz), 1.19–1.28 (m, 44H, –CH<sub>2</sub>), 1.59–1.64 (m, 4H, -CH<sub>2</sub>), 2.60–2.65 (m, 4H, -SO<sub>2</sub>CH<sub>2</sub>), 7.60 (m, 6H, Ph-H), 7.84 (m, 4H, Ph-H), 9.24 (d, 4H, Pv–H, J = 5.4 Hz), 9.37 (d, 4H, Pv–H, J = 5.7 Hz). <sup>13</sup>C–NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$ 14.26, 22.82, 25.34, 29.08, 29.50, 29.57, 29.72, 29.84, 32.05, 52.11, 124.35, 128.68, 130.92, 131.94, 142.39, 145.58, 150.05. ESI-HRMS (+ve): m/z calcd for C<sub>22</sub>H<sub>18</sub>N<sub>2</sub>: 155.0730 [M<sup>2+</sup>/2z]; found: 155.0723. ESI-HRMS (-ve): m/z calcd for C<sub>14</sub>H<sub>29</sub>O<sub>3</sub>S: 277.1843 [M<sup>-</sup>]; found: 277.1830. Anal. calcd for C<sub>50</sub>H<sub>76</sub>N<sub>2</sub>O<sub>6</sub>S<sub>2</sub>•4H<sub>2</sub>O: C, 64.07; H, 9.03; N, 2.99; S, 6.84; found: C, 63.84; H, 9.18; N, 2.87; S, 6.68.

Synthesis of N,N'-bis(4-dodecoxyphenyl)-4,4'-bipyridinium dichloride 2-Cl (n = 12). A mixture of 4-dodecoxyaniline<sup>61</sup> (2.44 g, 8.8 mmol) and compound 3 (2.25 g, 4.0 mmol) dissolved in N,N-dimethylacetamide (40 mL) was stirred at 90–95 °C for 24 h. The product was formed. Ethyl acetate (40 mL) was added dropwise at temperature below 60 °C. The solids were collected. The products isolated as yellow powder 2-Cl were obtained after recrystallization from methanol. Yield

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74%; <sup>1</sup>H–NMR (300 MHz, CD<sub>3</sub>OD): δ 0.91 (t, 6H, –CH<sub>3</sub>, *J* = 6.6 Hz), 1.31–1.55 (m, <sup>D</sup>36H, <sup>10</sup>2CH<sub>2</sub>), <sup>03090A</sup>
1.81–1.90 (m, 4H, –CH<sub>2</sub>), 4.15 (t, 4H, –OCH<sub>2</sub>, *J* = 6.5 Hz), 7.30 (d, 4H, Ph–H, *J* = 9.0 Hz), 7.86 (d,
4H, Ph–H, *J* = 8.7 Hz), 8.88 (br, 4H, Py–H), 9.49 (br, 4H, Py–H). <sup>13</sup>C–NMR (75 MHz, CD<sub>3</sub>OD): δ
14.45, 23.74, 27.11, 30.20, 30.48, 30.73, 33.08, 69.98, 117.29, 126.88, 128.27, 136.73, 146.75,
151.09, 163.41.

General synthetic procedures of N,N'-bis(4-dodecoxyphenyl)-4,4'-bipyridinium salts 2-X (X = BF4, PF6, OTf, NTf2, RSO3, SCN).

N,N'-Bis(4-dodecoxyphenyl)-4,4'-bipyridinium di(tetrafluoroborate) 2-BF4 (n = 12). To the solution of **2-Cl** (187 mg, 0.25 mmol) dissolved in methanol/CH<sub>2</sub>Cl<sub>2</sub> (1/5, 30ml), sodium tetrafluoroborate 10% aqueous solution (3.0 mL, 2.7 mmol) was added. This reaction was monitored using TLC (Al<sub>2</sub>O<sub>3</sub>) with CH<sub>3</sub>OH/CH<sub>2</sub>Cl<sub>2</sub> (5/95) as eluent and the  $R_f \sim 0.5$  of the product was higher than the  $R_f \sim 0.1$  of **2-Cl**. The organic layer was passed through a short Al<sub>2</sub>O<sub>3</sub> flash column. The crude product was collected after solvents removed. The products 2-BF4, isolated as white powder were obtained after crystallization from isopropanol/ethyl acetate. Yield 95%; <sup>1</sup>H–NMR (300 MHz, CDCl<sub>3</sub>): δ 0.91 (t, 6H, -CH<sub>3</sub>, J = 6.5 Hz), 1.31–1.53 (m, 36H, -CH<sub>2</sub>), 1.81–1.88 (m, 4H, -CH<sub>2</sub>), 4.14 (t, 4H, -OCH<sub>2</sub>, J = 6.5 Hz), 7.29 (d, 4H, Ph–H, J = 8.7 Hz), 7.83 (d, 4H, Ph–H, J = 6.0 Hz), 8.82 (br, 4H, Py–H), 9.46 (br, 4H, Py–H). <sup>19</sup>F–NMR (282 MHz, CDCl<sub>3</sub>/CD<sub>3</sub>OD, ref C<sub>6</sub>F<sub>6</sub> = -164.9):  $\delta$ -153.57 and -153.62 (s, B–F). ESI–HRMS (+ve): m/z calcd for C<sub>46</sub>H<sub>66</sub>N<sub>2</sub>O<sub>2</sub>: 339.2557 [M<sup>2+</sup>/2z]; found: 339.2536. ESI-HRMS (-ve): m/z calcd. for BF<sub>4</sub>: 87.0035 [M<sup>-</sup>]; found: 87.0038. Anal. calcd for C<sub>46</sub>H<sub>66</sub>B<sub>2</sub>F<sub>8</sub>N<sub>2</sub>O<sub>2</sub>•4.5H<sub>2</sub>O: C, 59.17; H, 8.10; N, 3.00; found: C, 58.94; H, 7.46; N, 3.12. N,N'-Bis(4-dodecoxyphenyl)-4,4'-bipyridinium di(hexafluorophosphate) (2-PF<sub>6</sub>). White powder; <sup>1</sup>H–NMR (300 MHz, DMSO-d<sub>6</sub>): 0.86 (t, 6H, –CH<sub>3</sub>, *J* = 6.6 Hz), 1.26–1.45 (m, 36H, –CH<sub>2</sub>),  $1.75-1.80 \text{ (m, 4H, -CH<sub>2</sub>), 4.13 (t, 4H, -OCH<sub>2</sub>, <math>J = 6.3 \text{ Hz}$ ), 7.32 (d, 4H, Ph-H, J = 8.7 Hz), 7.90 (d, 4H, Ph–H, J = 7.5 Hz), 9.01 (br, 4H, Py–H), 9.62 (br, 4H, Py–H). <sup>19</sup>F–NMR (282 MHz, CD<sub>3</sub>OD, ref  $C_6F_6 = -164.9$ ):  $\delta -74.4$  (d, P-F, J = 707 Hz). ESI-HRMS (+ve): m/z calcd for  $C_{46}H_{66}N_2O_2$ : 339.2557 [M<sup>2+</sup>/2*z*]; found: 339.2527. ESI–HRMS (–ve): *m*/*z* calcd for F<sub>6</sub>P: 144.9647 [M<sup>-</sup>]; found:

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View Article Online 144.9644. Anal. calcd for C<sub>46</sub>H<sub>66</sub>F<sub>12</sub>N<sub>2</sub>O<sub>2</sub>P<sub>2</sub>•H<sub>2</sub>O: C, 55.98; H, 6.94; N, 2.84; found: C,<sup>5</sup>6.16,<sup>6</sup>F,<sup>7</sup>C<sup>03090A</sup> 6.87; N, 2.86.

N,N'-Bis(4-dodecoxyphenyl)-4,4'-bipyridinium di(trifluoromethanesulfonate) 2-OTf. White powder; <sup>1</sup>H–NMR (300 MHz, CD<sub>3</sub>OD):  $\delta$  0.91 (t, 6H, –CH<sub>3</sub>, *J* = 6.6 Hz), 1.31–1.55 (m, 36H, –CH<sub>2</sub>), 1.83–1.88 (m, 4H, –CH<sub>2</sub>), 4.14 (t, 4H, –OCH<sub>2</sub>, *J* = 6.3 Hz), 7.29 (d, 4H, Ph–H, *J* = 8.7 Hz), 7.84 (d, 4H, Ph–H, *J* = 8.1 Hz), 8.82 (br, 4H, Py–H), 9.47 (br, 4H, Py–H). <sup>19</sup>F–NMR (282 MHz, CD<sub>3</sub>OD, ref C<sub>6</sub>F<sub>6</sub> = –164.9):  $\delta$  –79.6 (s, C–F). ESI–HRMS (+ve): *m*/*z* calcd for C<sub>46</sub>H<sub>66</sub>N<sub>2</sub>O<sub>2</sub>: 339.2557 [M<sup>2+</sup>/2z]; found: 339.2535. ESI–HRMS (–ve): *m*/*z* calcd for CF<sub>3</sub>O<sub>3</sub>S: 148.9526 [M<sup>-</sup>]; found: 148.9520. Anal. calcd for C<sub>48</sub>H<sub>66</sub>F<sub>6</sub>N<sub>2</sub>O<sub>8</sub>S<sub>2</sub>: C, 59.00; H, 6.81; N, 2.87; found: C, 58.53; H, 6.89; N, 2.78.

N,N'-Bis(4-dodecoxyphenyl)-4,4'-bipyridinium di[bis(trifluoromethanesulfonic)imide] 2-NTf<sub>2</sub> (*n* = 12). Brilliantly yellow powder; <sup>1</sup>H–NMR (300 MHz, CD<sub>3</sub>OD):  $\delta$  0.91 (t, 6H, –CH<sub>3</sub>, *J* = 6.6 Hz), 1.31–1.55 (m, 36H, –CH<sub>2</sub>), 1.81–1.90 (m, 4H, –CH<sub>2</sub>), 4.14 (t, 4H, –OCH<sub>2</sub>, *J* = 6.5 Hz), 7.29 (d, 4H, Ph–H, *J* = 9.0 Hz), 7.82 (d, 4H, Ph–H, *J* = 8.7 Hz), 8.81 (br, 4H, Py–H), 9.46 (br, 4H, Py–H). <sup>19</sup>F–NMR (282 MHz, CD<sub>3</sub>OD, ref C<sub>6</sub>F<sub>6</sub> = –164.9):  $\delta$  –80.19 (s, C–F). ESI–HRMS (+ve): *m/z* calcd for C<sub>46</sub>H<sub>66</sub>N<sub>2</sub>O<sub>2</sub>: 339.2557 [M<sup>2+</sup>/2*z*]; found: 339.2547. ESI–HRMS (–ve): *m/z* calcd for C<sub>2</sub>F<sub>6</sub>NO<sub>4</sub>S<sub>2</sub>: 279.9178 [M<sup>-</sup>]; found: 279.9165. Anal. calcd for C<sub>50</sub>H<sub>66</sub>F<sub>12</sub>N<sub>4</sub>O<sub>10</sub>S<sub>4</sub>: C, 48.46; H, 5.37; N, 4.52; found: C, 48.13; H, 5.47; N, 4.33.

N,N'-Bis(4-decoxyphenyl)-4,4'-bipyridinium di[bis(trifluoromethanesulfonic)imide] 2-NTf<sub>2</sub> (*n* = 10). Brilliant yellow powder; <sup>1</sup>H–NMR (300 MHz, CD<sub>3</sub>OD):  $\delta$  0.91 (t, 6H, –CH<sub>3</sub>, *J* = 6.9 Hz), 1.32–1.53 (m, 28H, –CH<sub>2</sub>), 1.81–1.88 (m, 4H, –CH<sub>2</sub>), 4.14 (t, 4H, –OCH<sub>2</sub>, *J* = 6.3 Hz), 7.29 (d, 4H, Ph–H, *J* = 8.7 Hz), 7.82 (d, 4H, Ph–H, *J* = 8.1 Hz), 8.82 (br, 4H, Py–H), 9.47 (br, 4H, Py–H). <sup>19</sup>F–NMR (282 MHz, CD<sub>3</sub>OD, ref C<sub>6</sub>F<sub>6</sub> = –164.9):  $\delta$  –80.23 (s, C–F). ESI–HRMS (+ve): *m/z* calcd for C<sub>42</sub>H<sub>58</sub>N<sub>2</sub>O<sub>2</sub>: 311.2244 [M<sup>2+</sup>/2z]; found: 311.2223. ESI–HRMS (–ve): *m/z* calcd for C<sub>2</sub>F<sub>6</sub>NO<sub>4</sub>S<sub>2</sub>: 279.9178 [M<sup>-</sup>]; found: 279.9206. Anal. calcd for C<sub>46</sub>H<sub>58</sub>F<sub>12</sub>N<sub>4</sub>O<sub>10</sub>S<sub>4</sub>: C, 46.69; H, 4.94; N, 4.74; found: C, 46.74; H, 5.02; N, 4.71.

#### N,N'-Bis(4-tetradecoxyphenyl)-4,4'-bipyridinium di[bis(trifluoromethanesulfonic)imide]

**2-NTf<sub>2</sub>** (*n* = 14). Brilliant yellow powder; <sup>1</sup>H–NMR (300 MHz, CD<sub>3</sub>OD):  $\delta$  0.90 (t, 6H): <u>1</u>CH<sub>3</sub>/Cf<sub>2</sub>C<sub>3</sub>O<sub>3</sub>OD/A 7.2 Hz), 1.30–1.53 (m, 44H, –CH<sub>2</sub>), 1.81–1.88 (m, 4H, –CH<sub>2</sub>), 4.14 (t, 4H, –OCH<sub>2</sub>, *J* = 6.3 Hz), 7.29 (d, 4H, Ph–H, *J* = 9.0 Hz), 7.82 (d, 4H, Ph–H, *J* = 7.2 Hz), 8.82 (br, 4H, Py–H), 9.47 (br, 4H, Py–H). <sup>19</sup>F–NMR (282 MHz, CD<sub>3</sub>OD, ref C<sub>6</sub>F<sub>6</sub> = –164.9):  $\delta$  –80.23 (s, C–F). ESI–HRMS (+ve): *m/z* calcd for C<sub>50</sub>H<sub>74</sub>N<sub>2</sub>O<sub>2</sub>: 367.2870 [M<sup>2+</sup>/2z]; found: 367.2848. ESI–HRMS (–ve): *m/z* calcd for C<sub>2</sub>F<sub>6</sub>NO4S<sub>2</sub>: 279.9178 [M<sup>-</sup>]; found: 279.9176. Anal. calcd for C<sub>54</sub>H<sub>74</sub>F<sub>12</sub>N<sub>4</sub>O<sub>10</sub>S<sub>4</sub>: C, 50.07; H, 5.76; N, 4.32; found: C, 50.12; H, 5.81; N, 4.34.

N,N'-Bis(4-dodecoxyphenyl)-4,4'-bipyridinium di(1-dodecylsulfonate) 2-RSO<sub>3</sub> (n = 12). Yellow powder; <sup>1</sup>H–NMR (300 MHz, CD<sub>3</sub>OD): δ 0.91 (m, 12H, –CH<sub>3</sub>), 1.29–1.53 (m, 72H, –CH<sub>2</sub>), 1.71–1.88 (m, 8H, –CH<sub>2</sub>), 2.73–2.79 (m, 4H, SO<sub>2</sub>–CH<sub>2</sub>), 4.15 (t, 4H, –OCH<sub>2</sub>, J = 6.3 Hz), 7.30 (d, 4H, Ph-H, J = 8.4 Hz), 7.85 (d, 4H, Ph-H, J = 7.8 Hz), 8.85 (br, 4H, Pv-H), 9.49 (br, 4H, Pv-H). ESI-HRMS (+ve): *m*/*z* calcd for C<sub>46</sub>H<sub>66</sub>N<sub>2</sub>O<sub>2</sub>: 339.2557 [M<sup>2+</sup>/2*z*]; found: 339.2545. ESI-HRMS (-ve): *m/z* calcd for C<sub>12</sub>H<sub>25</sub>O<sub>3</sub>S: 249.1530 [M<sup>-</sup>]; found: 249.1519. Anal. calcd for C<sub>70</sub>H<sub>116</sub>N<sub>2</sub>O<sub>8</sub>S<sub>2</sub>•4H<sub>2</sub>O: C, 67.27; H, 10.00; N, 2.24; found: C, 67.42; H, 10.10; N, 2.26. N,N'-Bis(4-decoxyphenyl)-4,4'-bipyridinium di(1-decylsulfonate) 2-RSO<sub>3</sub> (*n* = 10). Yellow powder;  ${}^{1}H-NMR$  (300 MHz, CDCl<sub>3</sub>):  $\delta$  0.90 (m, 12H, -CH<sub>3</sub>), 1.28-1.45 (m, 56H, -CH<sub>2</sub>), 1.65-1.83 (m, 8H,  $-CH_2$ ), 2.68-2.73 (m, 4H, SO<sub>2</sub>-CH<sub>2</sub>), 3.94 (t, 4H,  $-OCH_2$ , J = 6.3 Hz), 7.02 (d, 4H, Ph–H, J = 9.0 Hz), 7.75 (d, 4H, Ph–H, J = 8.7 Hz), 9.16 (d, 4H, Py–H, J = 5.7 Hz), 9.36 (d, 4H, Py-H, J = 5.7 Hz). <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>): δ 14.24, 22.81, 25.40, 26.12, 29.12, 29.23, 29.48, 29.60, 29.74, 32.03, 52.17, 68.95, 116.36, 125.45, 128.31, 134.75, 145.06, 148.68, 161.89. ESI-HRMS (+ve): m/z calcd for C<sub>42</sub>H<sub>58</sub>N<sub>2</sub>O<sub>2</sub>: 311.2244 [M<sup>+</sup>/2z]; found: 311.2223. ESI-HRMS (-ve): m/z calcd for C<sub>10</sub>H<sub>21</sub>O<sub>3</sub>S: 221.1217 [M<sup>-</sup>]; found: 221.1212. Anal. calcd for C<sub>62</sub>H<sub>100</sub>N<sub>2</sub>O<sub>8</sub>S<sub>2</sub>•4H<sub>2</sub>O: C, 65.46; H, 9.57; N, 2.46; found: C, 65.47; H, 9.81; N, 2.43.

N,N'-Bis(4-tetradecoxyphenyl)-4,4'-bipyridinium di(1-tetradecylsulfonate) 2-RSO<sub>3</sub> (*n* = 14). Yellow powder; <sup>1</sup>H–NMR (300 MHz, CD<sub>3</sub>OD): δ 0.90 (m, 12H, –CH<sub>3</sub>), 1.30–1.53 (m, 88H, –CH<sub>2</sub>), 1.81–1.88 (m, 8H, –CH<sub>2</sub>), 2.73–2.79 (m, 4H, SO<sub>2</sub>–CH<sub>2</sub>), 4.14 (t, 4H, –OCH<sub>2</sub>, *J* = 6.3 Hz), 7.29 (d,

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4H, Ph–H, J = 9.0 Hz), 7.83 (d, 4H, Ph–H, J = 7.2 Hz), 8.82 (br, 4H, Py–H), 9.47 (br, P4H, P32/H); CO3090A ESI–HRMS (+ve): m/z calcd for C<sub>50</sub>H<sub>74</sub>N<sub>2</sub>O<sub>2</sub>: 367.2870 [M<sup>2+</sup>/2z]; found: 367.2854. ESI–HRMS (-ve): m/z calcd for C<sub>14</sub>H<sub>29</sub>O<sub>3</sub>S: 277.1843 [M<sup>-</sup>]; found: 277.1834. Anal. calcd for C<sub>78</sub>H<sub>132</sub>N<sub>2</sub>O<sub>8</sub>S<sub>2</sub>•4H<sub>2</sub>O: C, 68.78; H, 10.36; N, 2.06; found: C, 68.88; H, 10.68; N, 2.03. **N,N'-Bis(4-dodecoxyphenyl)-4,4'-bipyridinium di(thiocyanate) 2-SCN.** Orange powder; <sup>1</sup>H–NMR (300 MHz, CDCl<sub>3</sub>/CD<sub>3</sub>OD co-solvent): 0.79 (t, 6H, –CH<sub>3</sub>, J = 6.9 Hz), 1.19–1.40 (m, 36H, –CH<sub>2</sub>), 1.74–1.78 (m, 4H, –CH<sub>2</sub>), 3.99 (t, 4H, –OCH<sub>2</sub>, J = 6.6 Hz), 7.10 (d, 4H, Ph–H, J = 9.0 Hz), 7.71 (d, 4H, Ph–H, J = 8.1 Hz), 8.89 (br, 4H, Py–H), 9.19 (br, 4H, Py–H). ESI–HRMS (+ve): m/zcalcd for C<sub>46</sub>H<sub>66</sub>N<sub>2</sub>O<sub>2</sub>: 339.2557 [M<sup>2+</sup>/2z]; found: 339.2547. ESI–HRMS (–ve): m/z calcd for CNS: 57.9757 [M<sup>-</sup>]; found: 57.9767. Anal. calcd for C<sub>48</sub>H<sub>66</sub>N<sub>4</sub>O<sub>2</sub>S<sub>2</sub>•2H<sub>2</sub>O: C, 69.36; H, 8.49; N, 6.74; found: C, 69.40; H, 8.51; N, 6.82.

## **IV. Conclusions**

In summary, thermal behaviors of the divalent ILCs with rigid core of diphenylviologens **1-2** were investated. Supported by the crystal packing analysis using single crystal-XRD, all alkyl chains of vilogen **1-RSO**<sub>3</sub> with bilayered lamellar structure and alkoxy chains of viologen **2-BF**<sub>4</sub> with monolayered lamellar structure are highly interdigitated. H-bonds generating between bipyridinium and counter anion were observed. The lamellar thicknesses of viologens **1-2** confirmed in powder XRD are both carbon length and counter anion dependence. The wave lengthes of absorption peaks for all viologens are negative solvatochromism corresponding to hypsochromic shif with increasing solvent polarity. AIE found in viologen **2-X** (*e.g.*, X = NTf<sub>2</sub>) plays as a role as the thermal switch with On/Off-emission mode between crystal and SmA phases. For the electrochemical properties of viologens, spike–like voltammetric peaks exhibiting on votammograms may be caused by the long chain containing viologen to form a 2D condensed film on the graphite cathode surface.

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