

## Supporting Information

## Experimental Section

### Materials and reagents

1,8-naphthalic anhydride, 1-(2-ethyl)bromohexane, 1-bromooctane and 1-bromo-hexadecane was purchased from Aladdin. 1-(2-hexyl)decanol and 1-(2-decyl)tetradecanol were purchased from Sigma-Aldrich. Triphenylphosphine (TPP) and carbon tetrabromide (CBr<sub>4</sub>) were purchased from Sinopharm Chemical Reagent Co.,Ltd. Organic solvents used during synthesis and purification, including methanol, dichloromethane (DCM), N,N-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), tetrahydrofuran (THF), *n*-hexane and ammonia water (25%-28%), were obtained from Kermel (AR) Reagent. All these reagents were used without further purification. Water utilized was received from a UPH-IV ultrapure water apparatus (China) with a resistivity of 18.25 M-cm.

### Synthesis

#### *Synthesis of 1-(3-naphthalimidepropyl)imidazole*

1,8-naphthalic anhydride (4.95 g, 25 mmol) and 1-(3-aminopropyl)imidazole (6.26 g, 50 mmol) in DMF (200 mL) were stirred for 24 h at 90 °C. After the mixture was cooled to room temperature, 400 mL water was added. The mixture was put into a refrigerator and kept at 0 °C overnight. The crystals were gathered by filtration and thoroughly washed with excess water. Finally, the product was dried in vacuum to get an orange solid (7.47 g, yield: 98%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 8.62 (d, 2H), 8.24 (d, 2H), 7.78 (t, 2H), 7.62 (s, 1H), 7.07 (s, 1H), 7.04 (s, 1H), 4.26 (t, 2H), 4.10 (t, 2H), 2.26 (m, 2H). ESI-MS *m/z*: [M+H]<sup>+</sup> calculated: 306.12 found: 306.16. FTIR (KBr, wavenumber [cm<sup>-1</sup>]): 3137.3 (m, ν<sub>Ar</sub>(C-H)), 3081.3 (m, ν<sub>Ar</sub>(C-H)), 2935.7 (w, ν<sub>Al</sub>(C-H)), 2884.6 (w, ν<sub>Al</sub>(C-H)), 1868.1, (w) 1695.5 (s, ν(C=O)), 1652.1 (s, ν(C=O)), 1587.4 (s), 1507.4 (m), 1440.9 (m), 1344.4 (m), 1287.5 (w), 1236.4 (s), 1171.8 (w), 1079.2 (m), 1043.5 (m), 907.5 (m), 844.8 (w), 778.3 (s), 728.1 (w), 669.3 (w), 625.9 (w), 540.1 (w).

#### *Synthesis of 1-(2-hexyl)bromodecane and 1-(2-decyl)bromotetradecane*

1-(2-hexyl)bromodecane and 1-(2-decyl)bromotetradecane were synthesized following similar procedures reported in our previous work.<sup>1</sup> In brief, TPP (6.3 g, 24 mmol) and CBr<sub>4</sub> (4.8 g, 14.4 mmol) were added into a three-necked bottle filled with N<sub>2</sub>, followed by the addition of 30 mL THF. Then a solution of 1-(2-hexyl)decanol (2.9 g, 12 mmol) or 1-(2-decyl)tetradecanol (4.25 g, 12 mmol) in THF (20 mL) was added, and the mixture was stirred with mechanical agitation for 30 min. The color of the mixture turned from light green to pale yellow. After that, the mixture was filtered and the filtrate was gathered. After the organic solvent was removed under reduced pressure, a yellow solid was obtained which was re-dispersed in *n*-hexane and filtered again. The colorless filtrate was gathered and concentrated by rotary evaporation to get the crude products, which were purified by column chromatography (silica gel, 100-200 meshes) with *n*-hexane as eluent. Finally, 3.04 g 1-(2-hexyl)bromodecane (yield: 83%) and 4.24 g 1-(2-decyl)bromotetradecane (yield 84.6%) were obtained as yellowish oils after solvent removal and total drying. The characterizations of 1-(2-hexyl)bromodecane and 1-(2-decyl)bromotetradecane were totally consistent with our previous results.<sup>1</sup>

#### *General procedures for the synthesis of 1-5*

A mixture of 1-(3-naphthalimidepropyl)imidazole and corresponding alkyl halide in DMF was stirred for 72 h at 90 °C. After the mixture was cooled to room temperature, DMF was removed under reduced pressure. The viscous mixture was re-dissolved in a small amount of DCM and purified by column chromatography (silica gel, 100-200 meshes) using a methanol/DCM/ammonia water ternary mixture as eluent. The volume ratio is 10:90:1 in the synthesis of **1**, while 8:92:1 for the synthesis of **2-5**. After that, the solvent was removed under reduced pressure and the products were dried in vacuum for 24h at 45 °C. Before characterizations, the compounds were kept in a desiccator to prevent the re-absorption of moisture in the air.

**1** (1-(3-naphthalimidepropyl)-3-(2-ethyl)hexylimidazolium bromide): 0.915 g (3 mmol) 1-(3-

naphthalimidepropyl)imidazole and 2.9 g (15 mmol) 1-(2-ethyl)bromohexane in 10 mL DMF were used as the starting material. Yield: 1.08 g (72.4%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 10.48 (s, 1H), 8.55 (d, 2H), 8.23 (d, 2H), 7.76 (t, 2H), 7.73 (s, 1H), 7.35 (s, 1H), 4.52 (t, 2H), 4.30 (d, 2H), 4.22 (t, 2H), 2.45 (m, 2H), 1.94 (m, 1H), 1.39 (m, 2H), 1.30 (m, 6H), 0.95 (t, 3H), 0.89 (t, 3H). <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>): 10.4, 14.0, 22.9, 23.3, 28.4, 29.1 30.0, 36.8, 40.1, 47.9, 53.6, 122.0, 122.2, 122.6, 127.0, 128.0, 131.5, 131.5, 134.4, 137.8, 164.3. ESI-MS m/z: [M]<sup>+</sup> calculated: 418.25 found: 418.23

**2** (1-(3-naphthalimidepropyl)-3-(2-hexyl)decylimidazolium bromide): 0.915 g (3 mmol) 1-(3-naphthalimidepropyl)imidazole and 1.89 g (6 mmol) 1-(2-hexyl)bromodecane in 10 mL DMF were used as the starting material. Yield: 0.895 g (48.9%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 10.61 (s, 1H), 8.58 (d, 2H), 8.24 (d, 2H), 7.77 (t, 2H), 7.74 (s, 1H), 7.25 (s, 1H), 4.52 (t, 2H), 4.29 (d, 2H), 4.23 (t, 2H), 2.45 (m, 2H), 1.96 (m, 1H), 1.26 (m, 24H), 0.86 (t, 3H), 0.84 (t, 3H). <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>): 14.1, 22.6, 26.2, 29.0, 29.3, 29.5, 29.8, 30.8, 31.8, 36.8, 38.9, 47.9, 54.1, 121.9, 122.1, 122.5, 127.0, 128.1, 131.5, 131.6, 134.4, 138.1, 164.3. ESI-MS m/z: [M]<sup>+</sup> calculated: 530.37 found: 530.38.

**3** (1-(3-naphthalimidepropyl)-3-(2-decyl)tetradecylimidazolium bromide): 0.915 g (3 mmol) 1-(3-naphthalimidepropyl)imidazole and 2.50 g (6 mmol) 1-(2-decyl)bromotetradecane in 10 mL DMF were used as the starting material. Yield: 1.26 g (58.2%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 10.67 (s, 1H), 8.60 (d, 2H), 8.26 (d, 2H), 7.78 (t, 2H), 7.70 (s, 1H), 7.21 (s, 1H), 4.51 (t, 2H), 4.29 (d, 2H), 4.24 (t, 2H), 2.45 (m, 2H), 1.96 (m, 1H), 1.22 (m, 40H), 0.87 (t, 3H), 0.86 (t, 3H). <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>): 14.1, 22.7, 26.2, 29.0, 29.3, 29.6, 29.7, 29.8, 30.8, 31.9, 36.8, 38.9, 47.9, 54.1, 121.8, 122.1, 122.4, 127.0, 128.1, 131.6, 131.6, 134.4, 138.1, 164.4. ESI-MS m/z: [M]<sup>+</sup> calculated: 642.50 found: 642.48.

**1'** (1-(3-naphthalimidepropyl)-3-oxylimidazolium bromide): 1.22 g (4 mmol) 1-(3-

naphthalimidepropyl)imidazole and 3.86 g (20 mmol) 1-bromooxane in 15 mL DMF were used as the starting material. Yield: 1.62 g (81.1%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 10.70 (s, 1H), 8.59 (d, 2H), 8.24 (d, 2H), 7.77 (t, 2H), 7.67 (s, 1H), 7.32 (s, 1H), 4.49 (t, 2H), 4.40 (d, 2H), 4.24 (t, 2H), 2.45 (m, 2H), 1.96 (m, 2H), 1.26 (m, 10H), 0.87 (t, 3H). <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>): 14.1, 22.6, 26.3, 29.0, 30.3, 31.7, 47.8, 50.2, 121.9, 122.3, 122.7, 127.0, 127.8, 131.4, 131.4, 134.4, 136.9, 164.2. ESI-MS m/z: [M]<sup>+</sup> calculated: 418.25 found: 418.23.

**2'** (1-(3-naphthalimidepropyl)-3-hexadecylidazolium bromide): 1.22 g (4 mmol) 1-(3-naphthalimidepropyl)imidazole and 6.11 g (20 mmol) 1-bromo-hexadecane in 15 mL DMF were used as the starting material. Yield: 2.16 g (88.4%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): 10.70 (s, 1H), 8.59 (d, 2H), 8.24 (d, 2H), 7.77 (t, 2H), 7.67 (s, 1H), 7.32 (s, 1H), 4.50 (t, 2H), 4.40 (d, 2H), 4.24 (t, 2H), 2.45 (m, 2H), 1.96 (m, 2H), 1.24 (m, 26H), 0.88 (t, 3H). <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>): 14.1, 18.4, 22.7, 26.3, 26.9, 29.1, 29.4, 29.5, 29.7, 30.3, 31.9, 36.9, 47.8, 50.3, 58.2, 122.0, 121.1, 122.6, 127.0, 127.9, 131.4, 131.4, 134.4, 137.2, 164.3. ESI-MS m/z: [M]<sup>+</sup> calculated: 530.37 found: 530.35.

## Instruments and methods

Nuclear magnetic resonance (NMR) data were acquired on a Bruker AV400 spectrometer. Electrospray ionization-mass spectrometry (ESI-MS) data were obtained on a Agilent 6510Q-TOF. Thermogravimetric analysis (TGA) was performed on a TA SDT Q600 thermal analyzer from 20 °C to 800 °C with a heating rate of 10 °C·min<sup>-1</sup> under N<sub>2</sub> atmosphere. Differential scanning calorimetry (DSC) measurements were carried out on a TA DSCQ20. Temperature-dependent polarized optical microscopy (POM) observations were performed on an Axio Scope.A1 (Germany) microscope. The samples were first heating to the isotropic phase (~150 °C for **1** and ~200 °C for **2** and **3**), followed by cooling to the desired temperatures at different rates (1 °C·min<sup>-1</sup> for **1** and **2**, and 5 °C·min<sup>-1</sup> for **3**). X-ray diffraction (XRD) patterns were taken on a D8 ADVANCE (Germany

Bruker) diffractometer equipped with Cu K $\alpha$  radiation and a graphite monochromator. Small-angle X-ray scattering (SAXS) measurements were performed on a small-angle X-ray scattering instrument (SAXSess, Anton Paar) with a Cu K $\alpha$  X-ray generation. Fourier transform infrared (FTIR) spectra in KBr pellets were recorded on a VERTEX-70/70v spectrophotometer. Atomic force microscopy (AFM) observations of the spin-coated films were carried out with an Asylum Cypher ES in tapping mode, with a scan frequency of 1.0 Hz and resolution of 512 $\times$ 512 pixels. Samples were prepared by spin coating (300 rpm for 5s followed by 2000 rpm for 30 s) a solution of target compound in CH<sub>2</sub>Cl<sub>2</sub> (10  $\mu$ L, 10 mmol $\cdot$ L<sup>-1</sup>) on quartz plates (thickness: 1 mm, diameter: 1 cm) which were pretreated by plasma cleaning. To get the thickness of films, each sample was scratched with a fine-tipped tweezer to create a groove or an empty region.

### **Nonlinear optical evaluations**

Z-scan tests of the spin coated samples of each ionic compound were performed on a homemade optical measurement system employing two Rj-7620 as detectors.<sup>2</sup> A 1064 nm infrared laser was used, with a high repetition rate ( $f$ ) of 58 MHz and half-peak breadth of 1.5 ps. The specimens are placed on a track directed to the beam position, which is 80 mm distributed symmetrically in the both side of focus. A Gaussian beam with far field intensity is focused on the splitter prism, specimens and lens. The specimen would move on the track of Z-path, and the real-time changing of laser intensity is related to the position of sample, which caused an obvious variation of absorption/transmittance. The laser was converged by lens, partially absorbed by sample, and gained by detectors. The aperture between sample and receiver is free in open aperture Z-scan for only nonlinear absorption is required.

The data were analyzed using the model developed by Sheik-Bahae et al.<sup>3</sup> The transmittance (T) was expressed by an infinite series:

$$T = \sum_{m=0}^{\infty} \frac{-[q_0(z,0)]^m}{(m+1)^{1.5}}$$

Take the first three terms of the expression as the approximation, and the results of open aperture  $Z$ -scan measurement were polynomial fitted by the approximation:

$$T = 1 - \frac{A}{\left(1 + \left(\frac{x}{B}\right)^2\right) \times 2^{1.5}} + \frac{A}{\left(1 + \left(\frac{x}{B}\right)^2\right)^2 \times 3^{1.5}} - \frac{A}{\left(1 + \left(\frac{x}{B}\right)^2\right)^3 \times 4^{1.5}}$$

The factor  $A$  and  $B$  were obtained by polynomial fitting results, which was depended on the properties of samples.

$$A = \beta L_{eff} I_0$$

$\beta$  was third order nonlinear absorption coefficient, which was an important parameter of third order nonlinear property.  $L_{eff}$  was effective thickness, obtained by actual thickness of samples  $L$  and linear absorption  $\alpha$ :

$$L_{eff} = \frac{1 - e^{-\alpha L}}{\alpha}$$

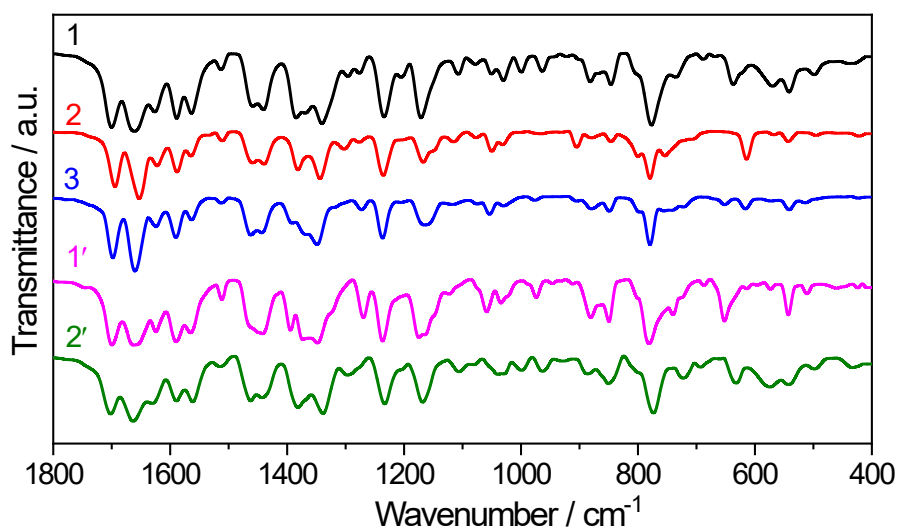
Actual thickness was gained by AFM measurements of the samples loaded on quartz plates, while linear absorption was obtained by spectrometers. Intensity of the light source  $I_0$ , calculated by fixed repetition rate and half-peak breadth, and practical waist radius and light source power:

$$I_0 = \frac{4 \ln \sqrt{2} \cdot \left(\frac{P}{f}\right)}{\pi^{1.5} \cdot \omega_0 \tau_{half}}$$

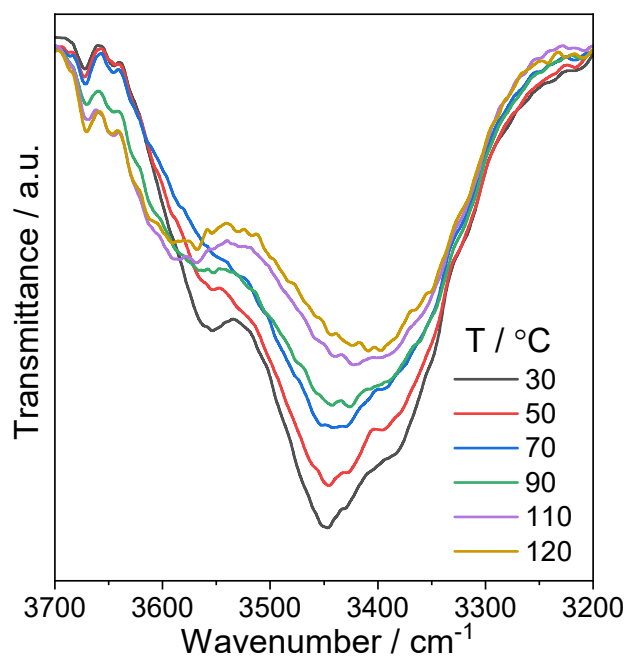
The repetition rate ( $f$ ) and half-peak breadth ( $\tau_{half}$ ) was fixed, and power was gained by oscilloscope, waist radius ( $\omega_0$ ) was got by the fitted value of factor  $B$  and light source  $\lambda$  (1064 nm):

$$B = \frac{\pi \omega_0^2}{\lambda}$$

Finally,  $\beta$  was obtained by the equations listed above.

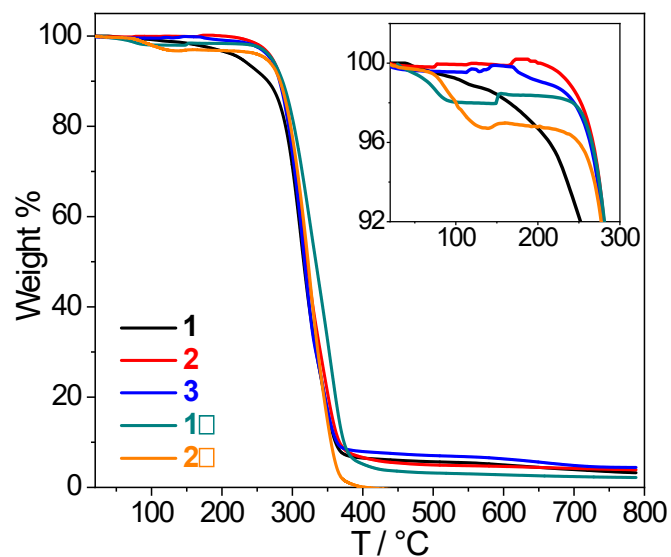


**Fig. S1** FTIR spectra of the five alkylated, naphthalimide-modified imidazolium bromides in a wavenumber range of 1800-400 cm<sup>-1</sup>.

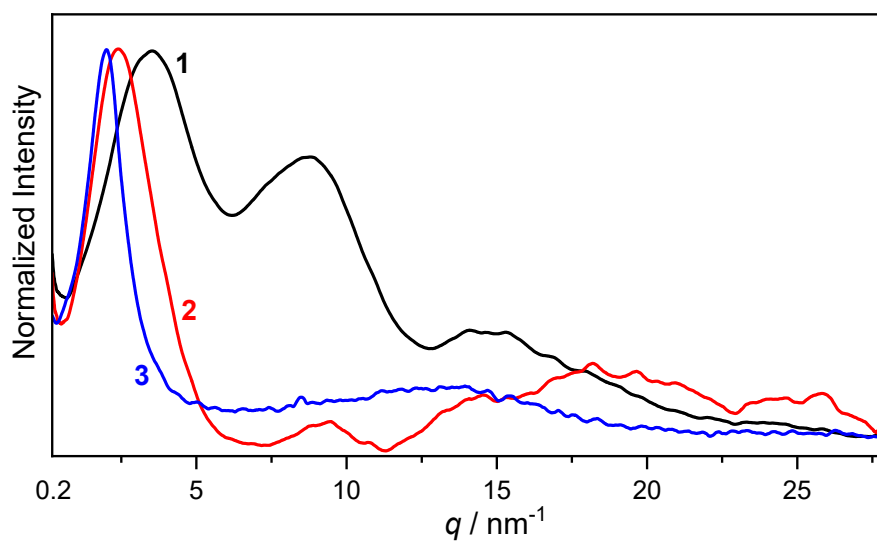


**Fig. S2** Temperature-dependent FTIR spectra of **1'** in a wavenumber range of 3700-3200 cm<sup>-1</sup>.

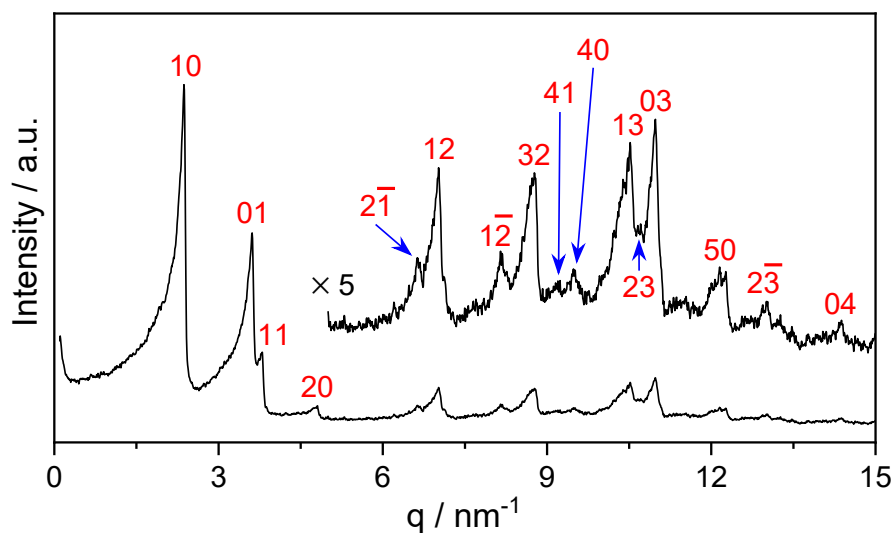




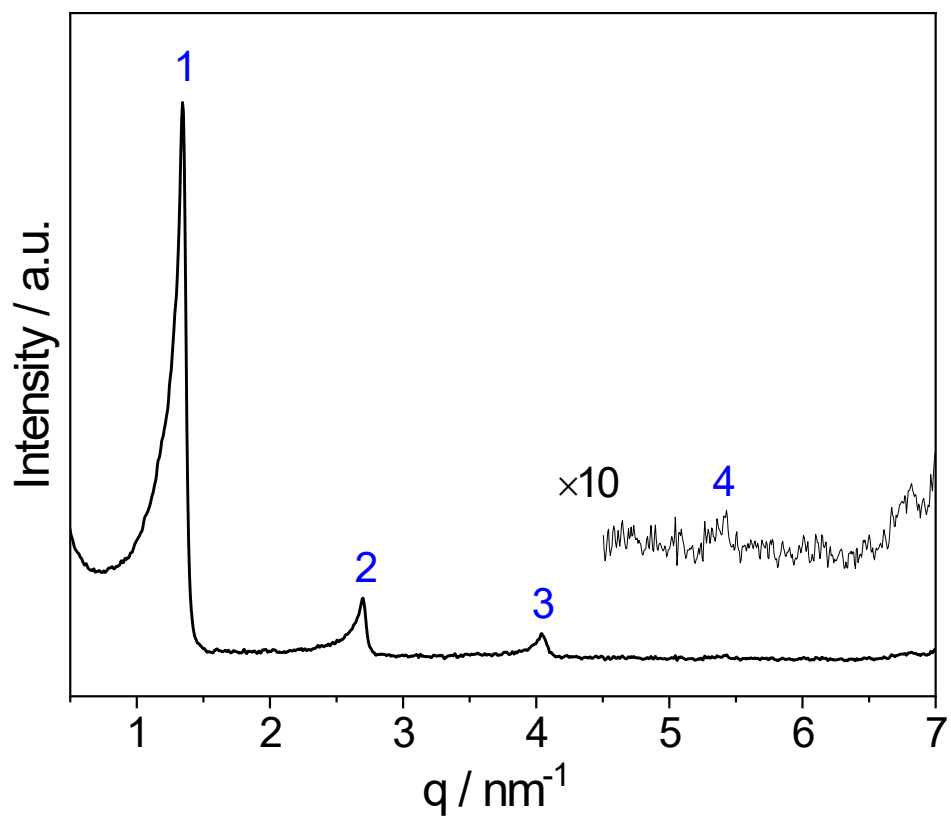
**Fig. S3** TGA curves of the five alkylated, naphthalimide-modified imidazolium bromides in a temperature range of 20-800 °C. Inset is the magnified curves before 300 °C.



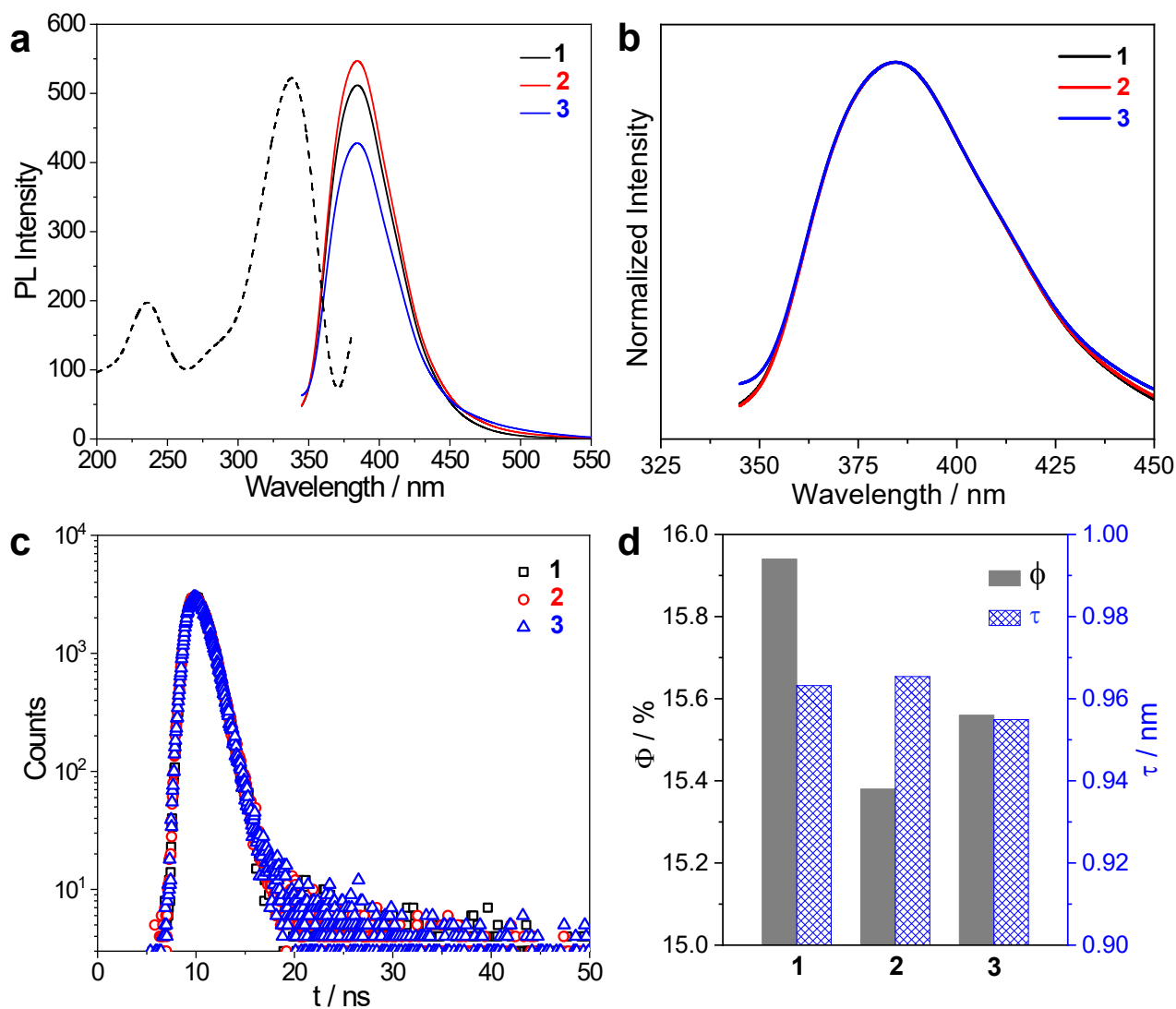
**Fig. S4** SAXS curves of 1-3 recorded above the  $T_m$ . Temperatures for the measurements are 110 °C for 1 and 185 °C for 2 and 3.



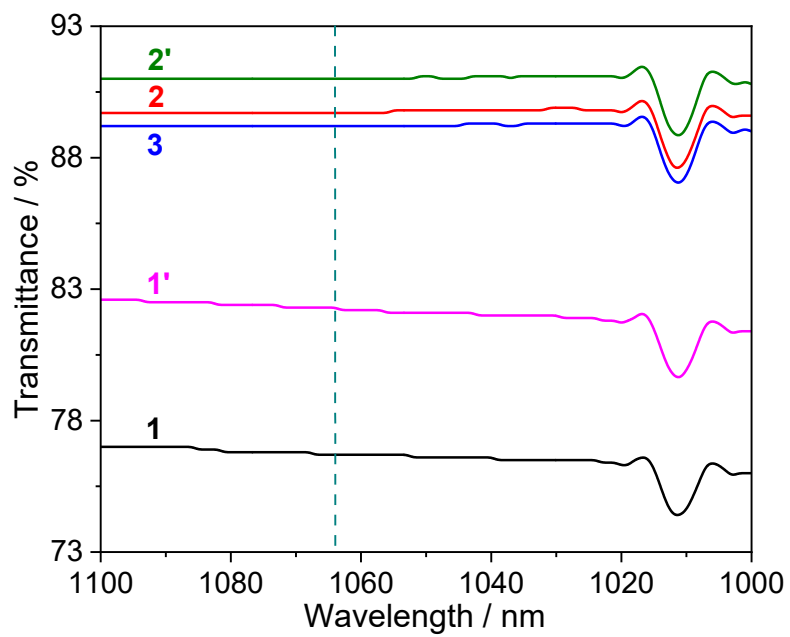
**Fig. S5** SAXS curve of **1'** recorded at 125 °C, which denotes the formation of a  $Col_o$  phase. Parameters of the lattice can be found in Table S3.



**Fig. S6** SAXS curve of **2'** recorded at 125 °C, which denotes the formation of a  $Sm$  phase.



**Fig. S7** a) Emission of the ethanol solutions of **1-3** with a concentration of  $0.5 \mu\text{mol}\cdot\text{L}^{-1}$ . the dashed line is the excitation of **1** at an emission of 385 nm. b) The emission curves shown in a after normalization of the intensity. c) The PL decays of **1-3**. d) Statistics of the fluorescence quantum yield ( $\phi$ ) and the lifetime of **1-3**. Note the very small ranges of the data on each y axis.



**Fig. S8** Transmittance of the spin-coated films from the five alkylated, naphthalimide-modified ionic compounds. The dashed line denotes the wavelength of the laser used in current study.

**Table S1.** Lattice parameters of the  $Col_o$  phase formed by **1** at 25 °C, which gives a system with  $a_o = 29.67 \text{ \AA}$ ,  $b_o = 27.53 \text{ \AA}$  and  $\gamma = 75^\circ$ .

$q \text{ (nm}^{-1}\text{)}$	$d_{\text{obs}} \text{ (\AA)}$	$hk$	$d_{\text{calcd}} \text{ (\AA)}$
2.19	28.69	10	28.69*
2.36	26.62	01	26.62*
2.77	22.60	11	22.60*
3.61	17.40	1-1	17.42
4.40	14.28	21	14.24
4.68	13.42	12	13.45
5.67	11.08	22	11.3
6.41	9.80	31	9.83
6.86	9.16	13	9.16

Calculated using LCDiXRay[3]. \* Data chosen for calculations

**Table S2.** Lattice parameters of the  $Col_l$  phase (C2mm) formed by **1** at 90 °C, which gives a system with  $a_r = 44.24 \text{ \AA}$  and  $b_r = 36.46 \text{ \AA}$ . Group conditions are:  $h + k = 2n$ ,  $h0=2n$  and  $0k=2n$ .

$q \text{ (nm}^{-1}\text{)}$	$d_{\text{obs}} \text{ (\AA)}$	$hk$	$d_{\text{calcd}} \text{ (\AA)}$
2.23	28.20	11	28.20*
2.87	21.89	20	22.1
3.44	18.30	02	18.30*
4.51	13.95	22	14.1
5.68	11.06	40	11.14
6.50	9.66	42	9.46
6.80	9.23	04	9.15

Calculated using LCDiXRay[3]. \* Data chosen for calculations

**Table S3.** Lattice parameters of the  $Col_0$  phase formed by **1'** at 125 °C, which gives a system with  $a_0 = 27.31 \text{ \AA}$ ,  $b_0 = 18.0 \text{ \AA}$  and  $\gamma = 75^\circ$ .

$q \text{ (nm}^{-1}\text{)}$	$d_{\text{obs}} \text{ (\AA)}$	$hk$	$d_{\text{calcd}} \text{ (\AA)}$
2.38	26.4	10	26.4*
3.61	17.40	01	17.40*
3.78	16.62	11	16.62*
4.79	13.11	20	13.2
6.65	9.44	2(-1)	9.41
7.0	8.97	12	8.98
8.15	7.70	1(-2)	7.70
8.76	7.17	32	7.17
9.22	6.81	41	6.77
9.50	6.61	40	6.60
10.51	5.97	13	5.99
10.70	5.87	23	5.89
10.98	5.78	03	5.8
12.16	5.16	43	5.04
12.96	4.83	2(-3)	4.87
14.44	4.35	04	4.35

Calculated using LCDiXRay[3]. \* Data chosen for calculations

## References

- 1 H. Zhu, G. Zhang, M. Chen, S. Zhou, G. Li, X. Wang, Q. Zhu, H. Li and J. Hao, *Chem. Eur. J.*, 2016, **22**, 6286-6293.
- 2 (a) S. Wang, Preparation and Properties of Different Dimensional Passive Optical Switches. *Dissertation for doctoral degree, Shandong University*; (b) K. Yin, D. Lu, W. Tian, R. Zhang, H. Yu, E. Gorecka, D. Pocięcha, N. Godbert, J. Hao and Hongguang Li. *J. Mater. Chem. C*, 2020, **8**, 8980-8991.
- 3 M. Sheik-Bahae, A. A. Said, T. H. Wei, D. J. Hagan and E. W. Stryland, *IEEE J. Quantum. Elect.*, 1990, **26**, 760-769.