Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

Supporting information (SI)

Ionic liquid crystals with Aggregation-Induced Emission Properties Based on Pyrrolo[3,2-b]pyrrole Salt Compounds

Zhe Peng,[a,b] Shuangxiong Dai,[a] Yingchun Ji, [a] Bin Tong,*[a] Jianbing Shi,[a] Zhengxu Cai,[a] Junge Zhi,[c] and Yuping Dong*[a]

[a] Beijing Key Laboratory of Construction Tailorable Advanced Functional Materials and Green Applications, College of Materials Science and Engineering, Beijing Institute of Technology, 5 South Zhongguancun Street, Beijing, 100081, China

[b] State Key Laboratory of Advanced Fiber Composites, Beijing Composite Materials Co., Ltd., Beijing, 102101, China.

[c] College of Science, Beijing Institute of Technology, Beijing 100081, China

* To whom correspondence should be addressed: Phone: +86-10-6891-7390; E-mail: tongbin@bit.edu.cn, chdongyp@bit.edu.cn.

Contents

S1. Synthesis and characterization of pyrrolo[3,2-b]pyrrole-based derivatives

The synthetic method for DPP-2Br is the same as reported earlier. [1] The synthetic procedures in detail are described below.

*Synthesis of 2,5-diphenyl-1,4-bis(4-(pyridin-4-yl)phenyl)-1,4-dihydropyrrolo[3,2-b]pyrrole (**DPP-2Py**).*

Under a nitrogen atmosphere, DPP-2Br (114 mg, 0.2 mmol), pyridine-4-boronic acid (73.8 mg, 0.6 mmol), tetrakis(triphenylphosphine)palladium(0) (12 mg, 0.01 mmol) and potassium carbonate (135 mg, 1 mmol) were added into a 100 mL two-necked round-bottom flask equipped with a magnetic stirrer and a condenser. 12 mL mixed solvent (toluene/methanol=3:1, v/v) with deoxygenization was added into round-bottom flask, and then the mixture was refluxed for more than 12 h (monitored by TLC). After cooling to room temperature, the mixture was washed with deionized water/dichloromethane three times, the organic layer was collected and dried. The products can be purified by column chromatography on silica gel (eluents, 1/1 ethyl acetate/ petroleum ether followed by ethyl acetate) to give 32 mg (28%) of DPP-2Py as a pale yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.67 (s, 4H), 7.67-7.64 (d, J = 8.42 Hz, 4H), 7.53-7.52 (d, J = 4.88 Hz, 4H), 7.42-7.40 (d, J = 8.41 Hz, 4H), 7.28-7.21 (m, 11H), 6.50 (s, 2H). MALDI-TOF m/z: calcd. for $C_{40}H_{28}N_4$: 564.7, found: 564.2 $[M]^+$.

4,4'-((2,5-diphenylpyrrolo[3,2-b]pyrrole-1,4-diyl)bis(4,1-phenylene))bis(1-nonylpyridin-1-ium) Iodine (DPP-2Py-9-I).

DPP-2Py (94 mg, 0.167 mmol), chloroform (25 mL) and 1-iodononane (330 μL, 1.67 mmol) were added into a 100 mL two-necked round-bottom flask equipped with a magnetic stirrer and a condenser, and then the mixture was heating at 80^{o}C and refluxed for 24 h. After cooling to room temperature, the solvent was removed by spin steaming. The product can be obtained to give 165 mg as a heavy red solid powder.

4,4'-((2,5-diphenylpyrrolo[3,2-b]pyrrole-1,4-diyl)bis(4,1-phenylene))bis(1-pentylpyridin-1-ium) Iodine (DPP-2Py-5-I).

The synthetic procedures of *DPP-2Py-5-I* were identical to that of *DPP-2Py-9-I.*

*4,4'-((2,5-diphenylpyrrolo[3,2-b]pyrrole-1,4-diyl)bis(4,1-phenylene))bis(1-nonylpyridin-1-ium) 4-toluenesulfonate (**DPP-2Py-9**).*

DPP-2Py-9-I (68 mg, 0.064 mmol), silver p-toluene sulphonate (106 mg, 0.38 mmol) and mixed solvents (methanol: water=14:1, v/v) were added into a 100 mL two-necked round-bottom flask equipped with a magnetic stirrer. The mixture was fully stirred for 8 h at 30^{o}C, and then filtrated to remove the black impurities. The crude product can be obtained by removing solvents. The target product can be purified by column chromatography on silica gel (eluent, dichloromethane: petroleum ether: methanol=10:10:1, v/v/v) to give 30 mg (40%) of DPP-2Py-9 as a red solid. ^{1}H NMR (400 MHz, CD_3OD, δ), 8.97-8.90 (s, 4H), 8.38-8.36 (d, J = 6.84 Hz, 4H), 8.06-8.04 (d, J = 8.65 Hz, 4H), 7.70-7.68 (d, J = 8.02 Hz, 4H), 7.52-7.50 (d, J = 8.63 Hz, 4H), 7.30-7.20 (m, 14H), 6.58 (s, 2H), 4.59-4.56 (t, J = 7.52 Hz, 4H), 2.32 (s, 6H), 1.40-1.30 (m, 28H), 0.91-0.88(t, J = 6.75 Hz, 6H). ^{13}C NMR (100 MHz, MeOD, δ): 155.29, 144.30, 143.50, 142.25, 140.24, 136.04, 133.25, 131.48, 130.46, 128.94, 128.43, 128.23, 128.09, 126.60, 125.56, 125.45, 124.26, 96.64, 60.73, 31.58, 30.99, 29.08, 28.91, 28.75, 25.83, 22.31, 19.93, 13.03. MS(ESI^+, direct infusion) m/z, 409.26$[M\text{-}2OTs^-]^{2+}$, MS (ESI^-, direct infusion): m/z, 171.01 $[OTs]^-$.

*4,4'-((2,5-diphenylpyrrolo[3,2-b]pyrrole-1,4-diyl)bis(4,1-phenylene))bis(1-pentylpyridin-1-ium) 4-toluenesulfonate (**DPP-2Py-5**).*

The synthetic procedures of *DPP-2Py-5* were identical to those of *DPP-2Py-9,* and the yellow solid was obtained finally with the yield of 38%. ^{1}H NMR (400 MHz, DMSO-d6, δ): 9.12-9.10 (d, J = 6.92 Hz, 4H), 8.55-8.53 (d, J = 6.91 Hz, 4H), 8.20-8.18 (d, J = 8.70 Hz, 4H), 7.53-7.47 (m, 10H), 7.33-7.31 (m, 10H), 7.12-7.10 (d, J = 7.88 Hz 6H), 6.69 (s, 2H), 4.59-4.56 (t, J = 7.27 Hz, 4H), 1.94 (s, 6H), 1.38-1.23 (m, 12H), 0.98-0.83(t, J = 7.08 Hz, 6H). ^{13}C NMR (100 MHz, DMSO-d6, δ): 153.92, 146.22, 145.18, 142.91, 138.06, 135.93, 133.25, 131.49, 130.79, 130.12, 129.88, 129.10, 128.51, 128.42, 127.36, 125.97, 125.76, 124.58, 97.68, 60.28, 30.79, 28.02, 22.06, 21.25, 14.23. MS (ESI^+, direct infusion) m/z, 353.20$[M\text{-}2OTs^-]^{2+}$, MS (ESI-, direct infusion): m/z, 171.01 $[OTs]^-$.

S2. Supplementary spectra data

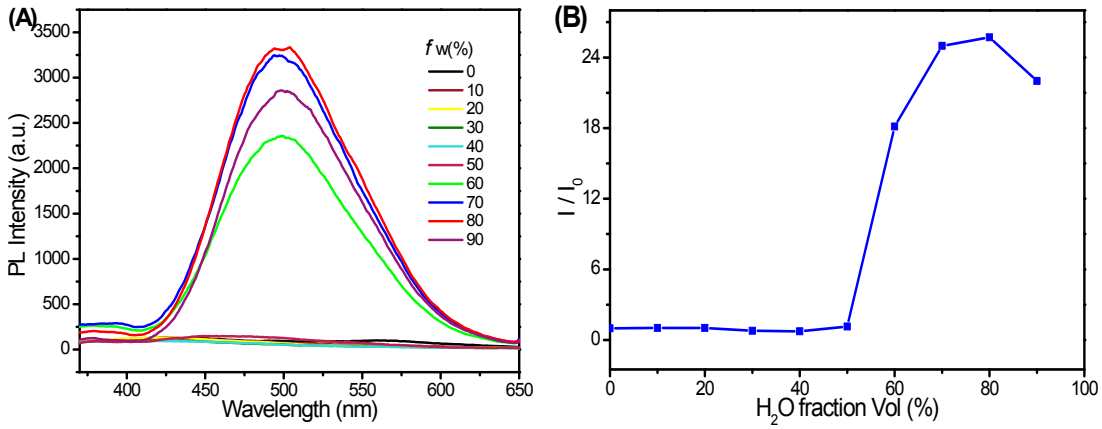

Fig. S1 (A) The emission spectra of DPP-2Py in DMSO/H_2O systems with different water fractions; (B) A plot of the ratio of maximum fluorescence intensity of DPP-2Py vs. fraction of water. (Concentration: 10^{-5} M; λ_{ex}: 325 nm)

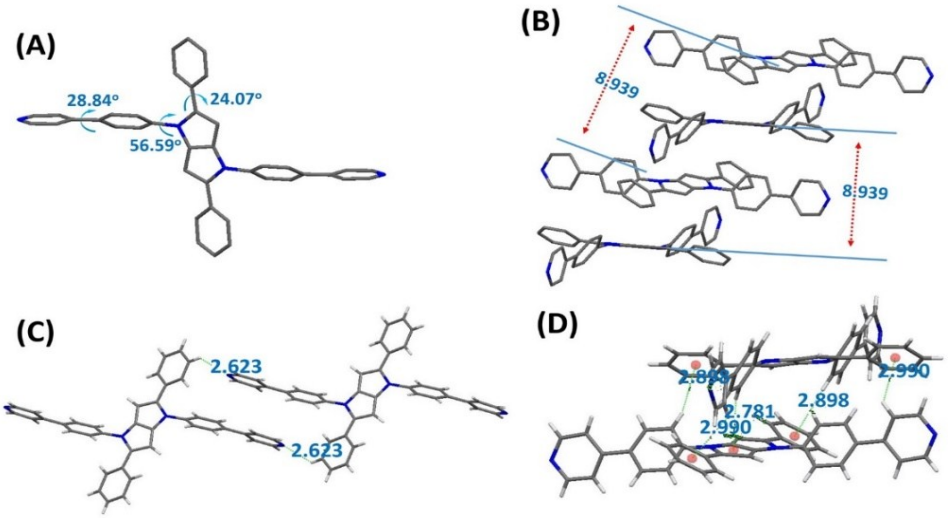

Fig. S2 The crystal structure (A), packing patterns (B) and intermolecular interactions with H-bonding (C) and CH-π (D) of DPP-2py.

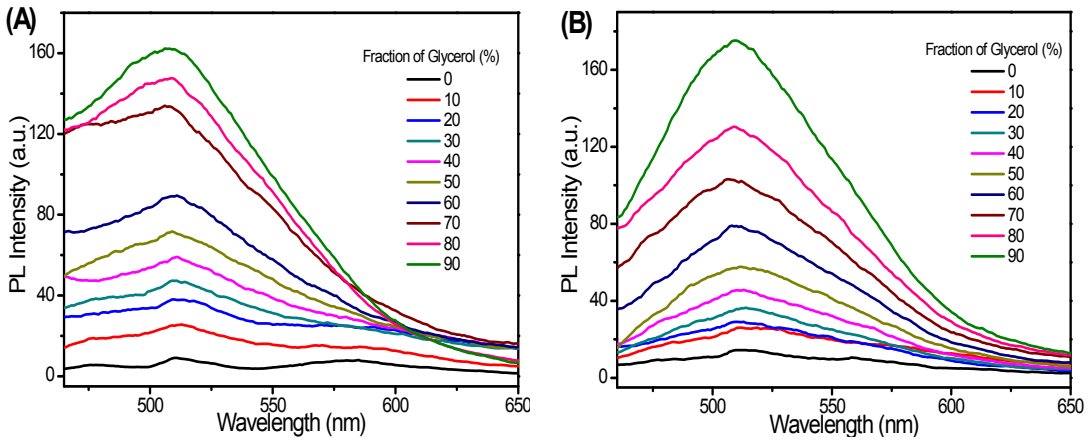

Fig. S3 The emission spectra of DPP-2Py-5 (A) and DPP-2Py-9 (B) in methanol/glycerol mixtures (Concentration: 10^{-5} M; λex: 440 nm)

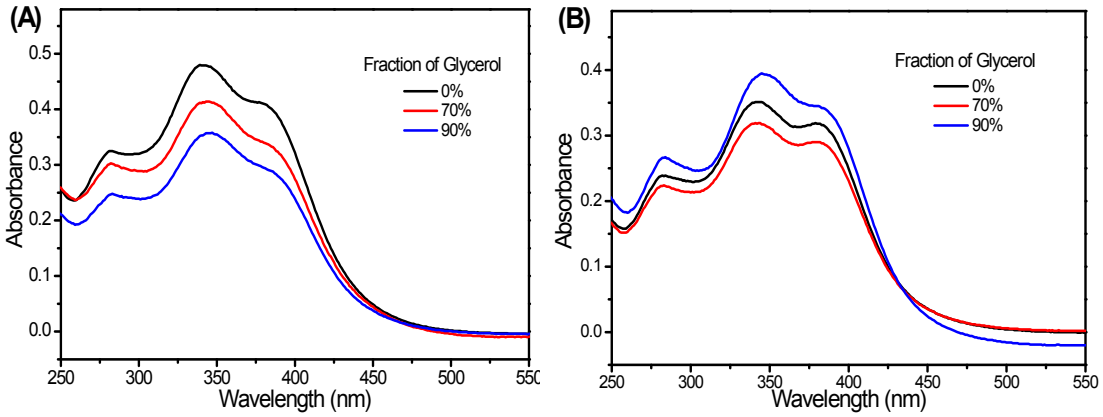

Fig. S4 The UV-vis absorption of DPP-2Py-5 (A) and DPP-2Py-9 (B) in f_G = 0, 70% and 90% of methanol/glycerol mixtures.

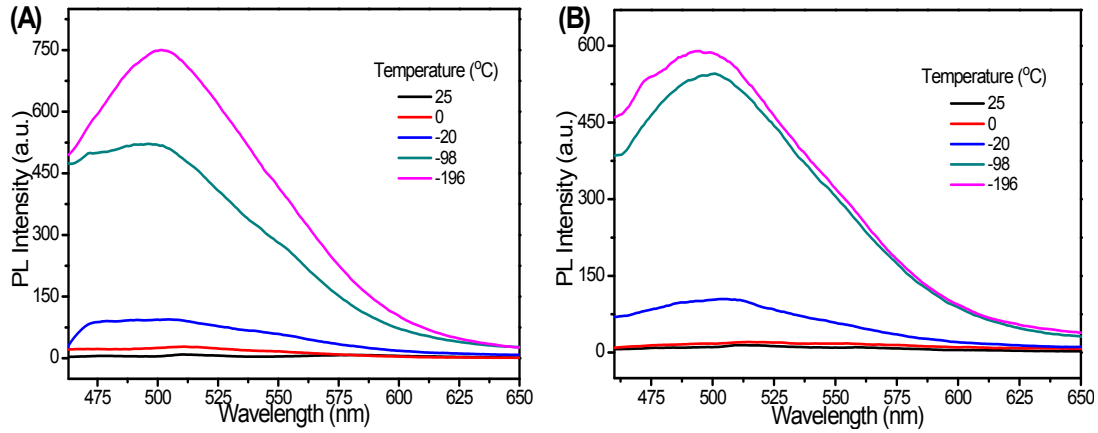

Fig. S5 The emission of DPP-2Py-5 (A) and DPP-2Py-9 (B) in methanol solution with different temperatures. (Concentration: 10^{-5} M; λex: 440 nm)

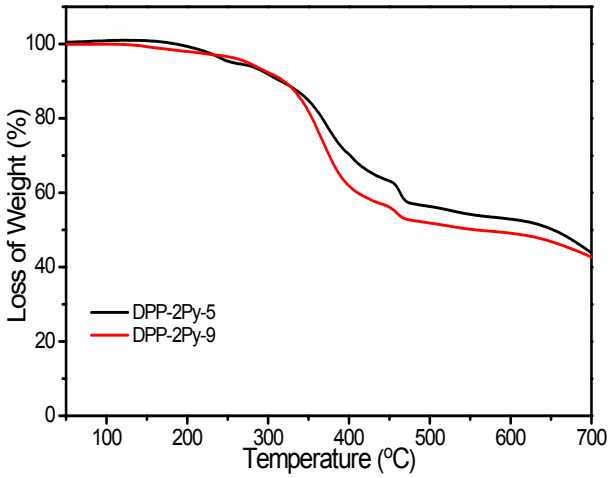

Fig. S6 The thermal properties of DPP-2Py-5 and DPP-2Py-9 characterized by thermogravimetric analysis (TGA).

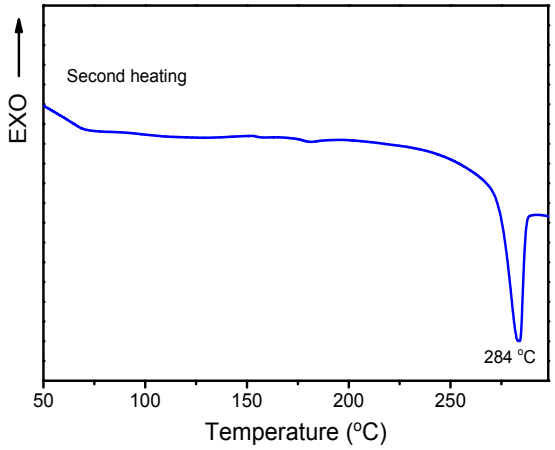

Fig. S7 The DSC curve of DPP-2py-5 in the second heating process.

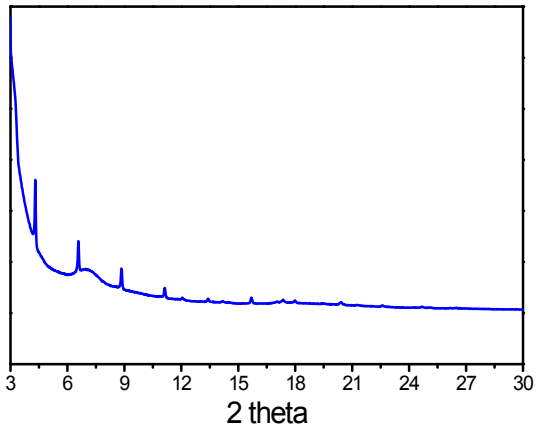

Fig. S8 XRD patterns of DPP-2Py-9 scanned at 185°C in second heating process.

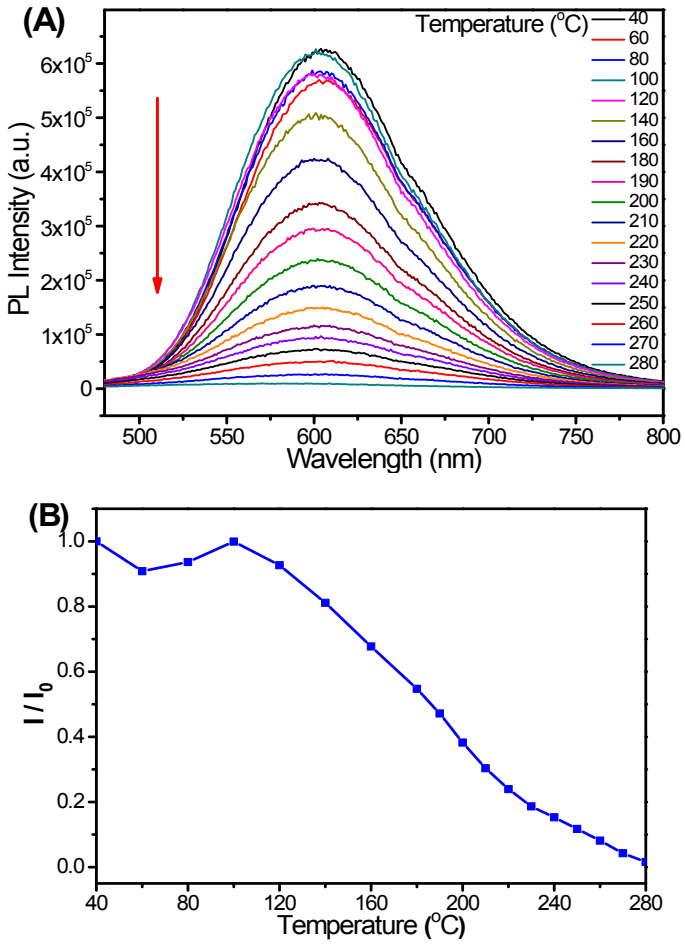

Fig. S9 The changes of fluorescence spectra of DPP-2Py-5 (A) and the ratio of maximum fluorescence intensity (B) as a function of temperature (λex: 440 nm).

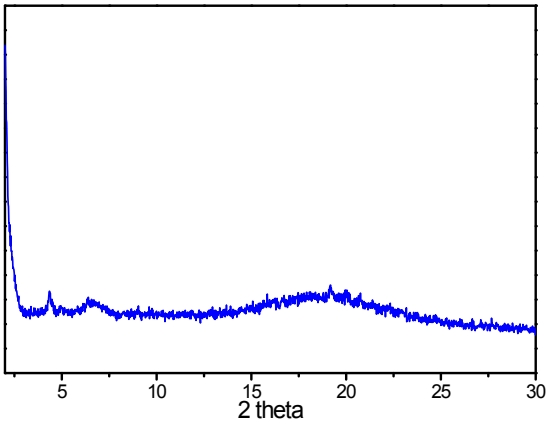

Fig. S10 The XRD curve of DPP-2Py-9 after heating treatment.

S3. Reference

[1] Z. Peng, Y. C. Ji, Z. Wang, B. Tong, J. B. Shi and Y. P. Dong, *Acta Chim. Sinica,* 2016, **74**, 942.