1. Materials

Unless otherwise noted, all starting materials, reagents, and solvents were obtained from commercial suppliers and were used without further purification. Analytical thin layer chromatography (TLC) was performed on glass silica gel plates; visualization of products was performed with a handheld UV lamp. All aqueous solutions were prepared with deionized distilled water obtained from a Milli-Q water-purifying system (18 MΩ cm).

2. Instruments and Measurements

The ^{1}H and ^{13}C NMR spectra were recorded on an AVANCE III 400MHz spectrometer using the residual solvent proton signal for calibration. Electrospray mass spectra were obtained on a Bruker maXis 4G ESI-Q-TOF. AFM imaging of samples prepared by dropping on a freshly cleaved mica were obtained on the Dimension FastScan Bio AFM. The HRTEM instrument used was a JEM-ARM200F equipped with a Gatan ONEVIEW CCD camera.

3. Synthesis The synthesis of compound **1** was shown in Figure S1. The precursor perylene monoanhydride (compound **2**) was synthesized according to the literature procedures.[S1, S2] The compound **3** was synthesized using literature procedures. [S3]

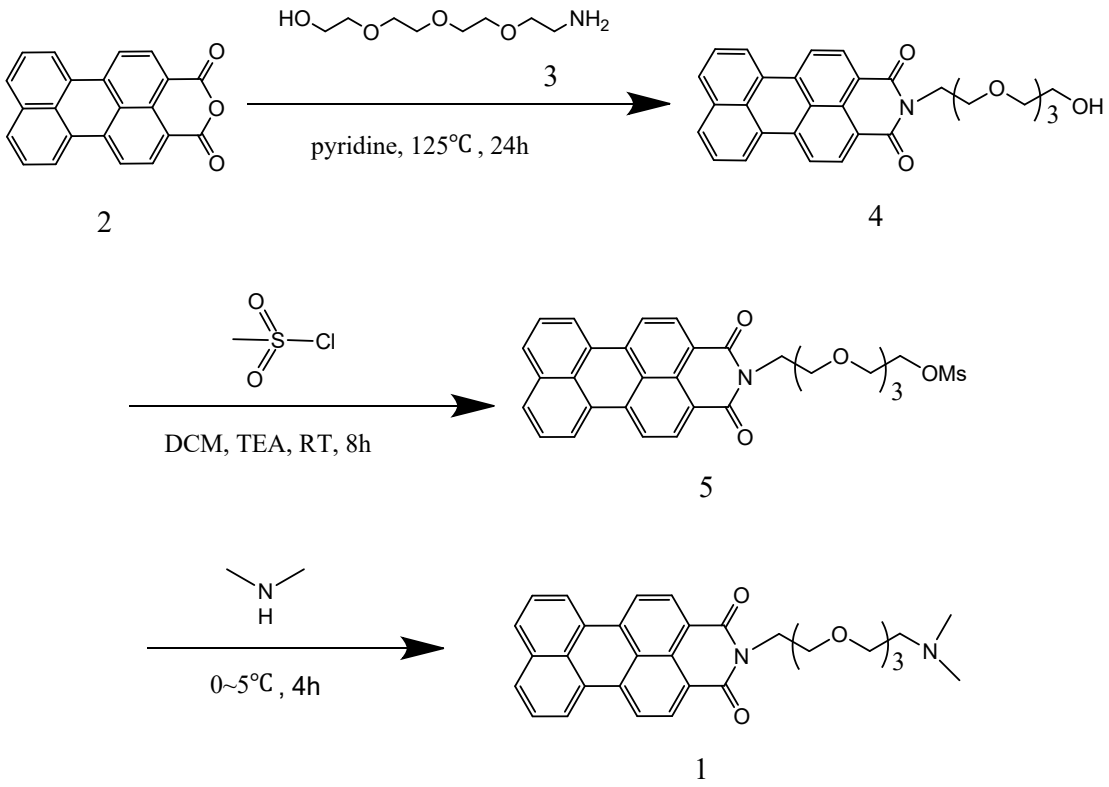

Fig. S1 The scheme for the synthesis of compound 1.

Compound 4. The compound **2** (322mg, 1mmol) and compound **3** (232mg, 1.2mmol) were dissolved in anhydrous pyridine (20 mL) at room temperature. The reaction mixture was heated at 125℃ for 24h under N_2. After completion of the reaction, DCM (30ml) was added to the mixture and the organic phase was washed with 2M HCl (3×20ml), followed by brine (3×20ml). The organic phase was dried over $MgSO_4$ and evaporated under vacuum to give compound **4** as a red solid. (Yield: about 95%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.26 (d, J = 8 Hz, 2H), 8.11 (d, J = 7.5 Hz, 2H), 8.01 (d, J = 8Hz, 2H), 7.76 (d, J = 8.0 Hz, 2H), 7.47 (t, J = 8.0 Hz ,2H), 4.40 (t, J = 6.5 Hz, 2H), 3.86 (t, J = 6 Hz, 2H), 3.76-3.56 (m, 12H). ^{13}C NMR (500 MHz, $CDCl_3$) δ 163.74, 136.75, 134.02, 131.11, 130.76, 129.38, 128.74, 127.44, 126.82, 126.24, 123.44, 120.42, 119.80, 72.47, 70.65, 70.37, 70.16, 68.01, 61.77, 39.05. MS (*m/z*): $[M+Na]^+$calcd for $[C_{30}H_{27}NNaO_6]$, 520.5; found: 520.6.

Compound 5. The compound **4** (340mg) and triethylamine (195 μl) were dissolved in anhydrous dichloromethane (20 ml). Methanesulfonyl chloride (130 μL) was added dropwise at 0 °C. The reaction mixture was then stirred for 8 h at room temperature. After completion of the reaction, the organic layer was washed with water, followed by 0.5 M HCl, saturated $NaHCO_3$ solution and brine. After treatment with anhydrous Na_2SO_4, the solvents were evaporated under vacuum to give 375 mg of the compound **5** (95% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.39 (d, J = 8.0 Hz, 2H), 8.24 (d, J = 7.5 Hz, 2H), 8.18 (d, J = 8.0 Hz, 2H), 7.83 (d, J = 8.0 Hz, 2H), 7.55 (t, J = 7.5 Hz, 2H), 4.44 (t, J = 6.0 Hz, 2H), 4.33 (m, 2H), 3.84 (t, J = 6.0 Hz, 2H), 3.75 – 3.69 (m, 4H), 3.65-3.58 (m, 6H), 3.07 (s, 3H). ^{13}C NMR (500 MHz, $CDCl_3$) δ 163.81, 137.01, 134.14, 131.31, 130.97, 129.60, 128.82, 127.65, 126.94, 126.41, 123.62, 120.57, 119.87, 70.56, 70.18, 69.31, 68.98, 67.98, 39.04, 37.68. MS (*m/z*): $[M+Na]^+$calcd for $[C_{31}H_{29}NNaO_8S]$, 598.57; found: 598.62.

Compound 1. A 60% solution of dimethylamine in water was slowly added to potassium hydroxide pellets with constant stirring at room temperature. The resultant dimethylamine was obtained by condensing the gaseous vapors in a side flask that was placed in a -10 to 0 ℃ dry ice/ethanol bath. Dimethylamine was added to compound **5** and the reaction mixture was stirred for about 4h at 0~5℃ under nitrogen. After completion of the reaction, the crude product was diluted with DCM and then extracted with water until the aqueous layer was neutral. The organic phase was dried over $MgSO_4$ and concentrated in vacuo by rotary evaporation. Purification via column chromatography (DCM: CH_3OH: NH_4OH=20:1:0.1) yielded the desired product as a dark red solid (Yield: 50%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (d, J = 8 Hz, 2H), 8.39 (d, J = 8 Hz, 2H), 8.35 (d, J = 8 Hz, 2H) 7.88 (d, J = 8.0 Hz, 2H), 7.61 (t, J = 8.0 Hz, 2H), 4.45 (t, J = 4 Hz, 8Hz, 2H), 3.85 (t, J = 4.0 Hz, 8.0Hz, 2H), 3.73 (t, J = 4.0 Hz, 8.0Hz, 2H), 3.67-3.52 (m, 8H), 2.59 (t, J = 4.0 Hz, 2H), 2.33 (s, 6H). ^{13}C NMR (500 MHz, $CDCl_3$) δ 163.54, 136.34, 133.86, 130.84,

130.63, 129.10, 128.51, 127.20, 126.68, 125.95, 123.25, 120.20, 119.46, 70.59, 70.53, 70.13, 68.64, 67.95, 58.43, 45.40, 38.99. MS (*m/z*): $[M+H]^+$ calcd for $[C_{32}H_{33}N_2O_5]$, 525.6; found: 525.4.

4. Crystal Structure Determination

Diffraction data of PMI•H^+Br^- were collected at BL17B of National Center for Shanghai Synchrotron Radiation Facility. Data reduction and absorption corrections were applied by using *HKL3000*. The structures were solved with the direct methods and refined with a full-matrix least-squares technique with the *SHELXTL* program package. Anisotropic thermal parameters were applied to all non-hydrogen atoms. The hydrogen atoms were generated geometrically. Crystal data as well as details of data collection and refinements for the compounds are summarized in Table S1.

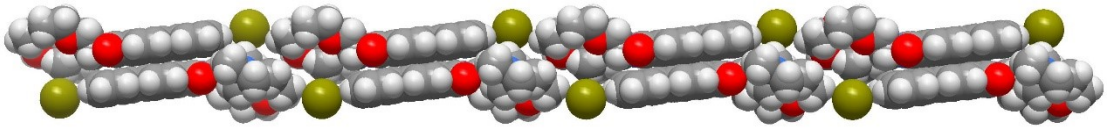

Fig. S2 X-ray crystal structure of the crystal packing of PMI•H^+Br^- viewed along the *a*-axis.

5. Powder X-ray diffraction

Powder X-ray diffraction (PXRD) patterns were recorded on a Bruker D8-Advance diffractometer using Cu Kα radiation and a LynxEye detector at room temperature.

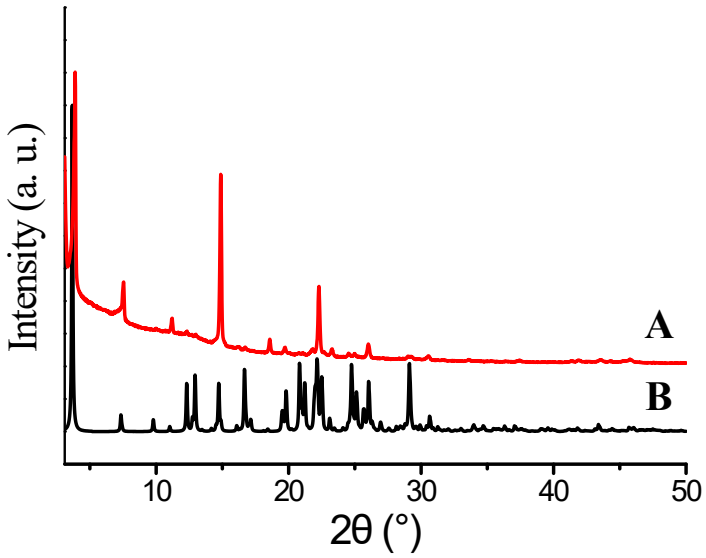

Fig. S3 PXRD patterns of (A) the as-synthesized PMI•H^+Br^-, and (B) simulated from single-crystal x-ray structure of the PMI•H^+Br^- system.

6. Determination of association constant of PMI•H^+ Cl^- and PMI•H^+ Br^-

2 mL of 0.01M host solution of PMI•HBF_4 were prepared in D_2O. Using the same solvents 1 mL of 0.1-0.5M stock solutions were prepared containing either nBu$_4$NCl or nBu$_4$NBr as anion source. Starting with 0.5 mL of the host solution, stock solution was added in small quantities and ^{1}H NMR spectra were recorded after each addition. The setup for the prepared solutions should enable the host concentration to stay almost constant throughout the measurements. Again the chemical shifts of the solvents were used as internal standard. The obtained data were plotted as relative chemical shift $\Delta\delta$ [ppm] at δ = 7.13 versus the anion concentration c(X^-) [mol/L] (calculated from NMR spectra). Fitting was done using nonlinear curve-fitting program afforded the corresponding association constants.

The non-linear curve-fitting was based on the equation:

$$\Delta\delta = (\Delta\delta_\infty/[H]_0)\ (0.5*X + 0.5([H]_0+1/K_a)-(0.5\ (X^2+(2*X(1/K_a - [H]_0)) + (1/K_a + [H]_0)^2)^{0.5})) \quad \text{(Eq. S1)}$$

Where $\Delta\delta$ is the relative chemical shift at X (the concentration of *Anion*), $\Delta\delta_\infty$ is the maximal relative chemical shift of the aromatic PMI proton when the host is completely complexed, $[H]_0$ is the fixed initial concentration of the binding partner H.[S4]

(a) (b)

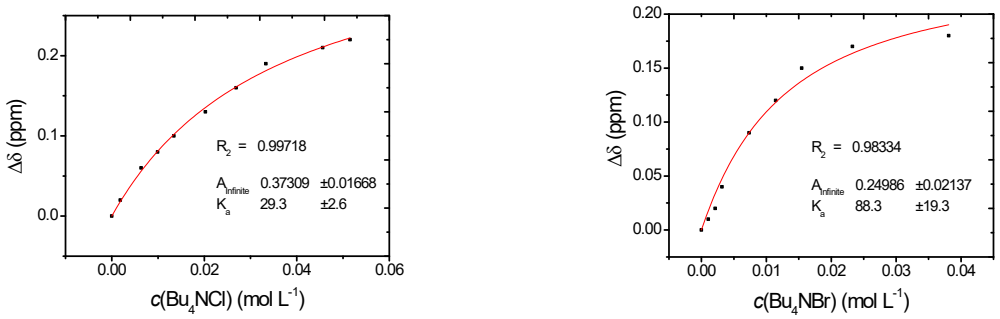

Fig. S4 The NMR shifts of PMIs-HBF_4 at δ = 7.13 upon addition of tetrabutylammonium chloride (a) or tetrabutylammonium bromine (b) in D_2O, respectively. The red solid lines were obtained from the non-linear curve-fitting using Eq. S1.

7. Absorption and Emission Spectroscopy

Electronic absorption spectra were recorded on a JASCO model V–570 UV/VIS/NIR spectrophotometer. The excitation and emission spectra were recorded at room temperature, with SHIMADZU RF-5301 PC luminescence spectrophotometer.

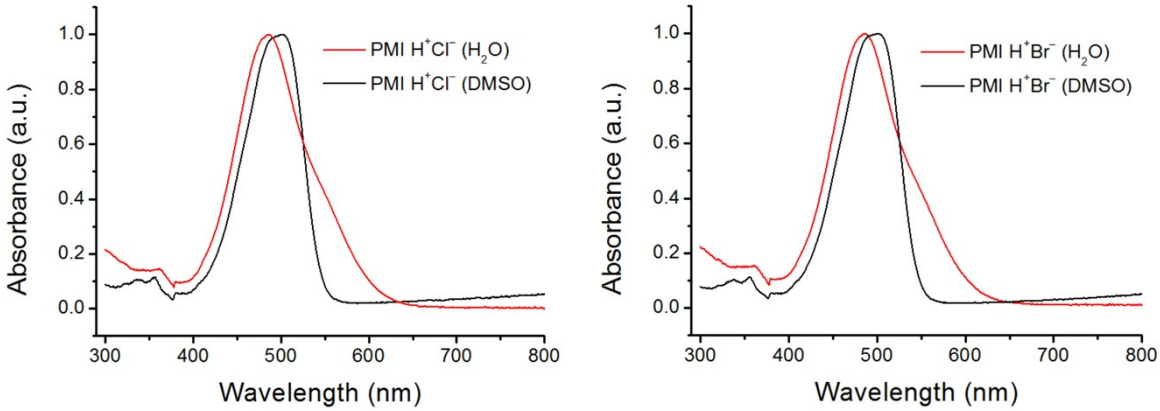

Fig. S5 Absorption spectra of PMI•H$^+$X$^-$ (X$^-$ = Cl$^-$ or Br$^-$) in DMSO and in water.

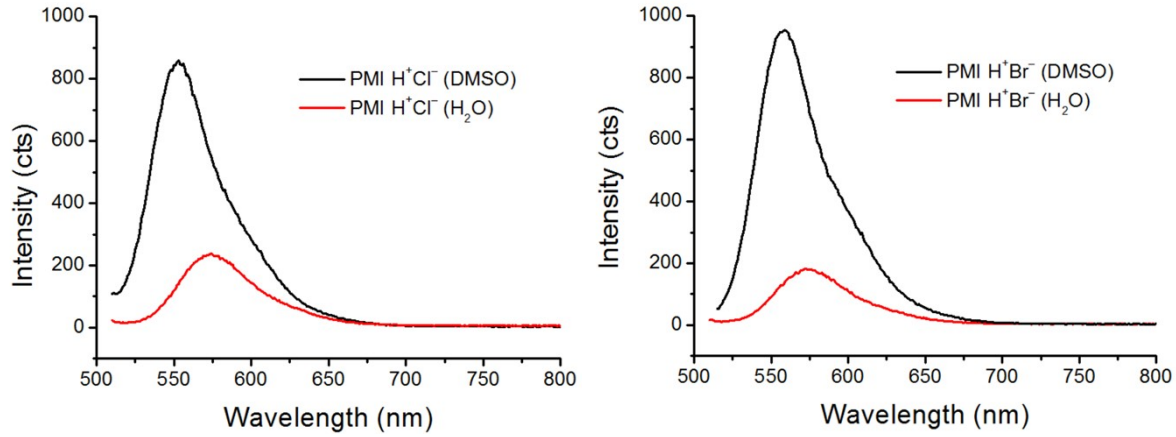

Fig. S6 Emission spectra of PMI•H$^+$X$^-$ (X$^-$ = Cl$^-$ or Br$^-$) in DMSO and in water.

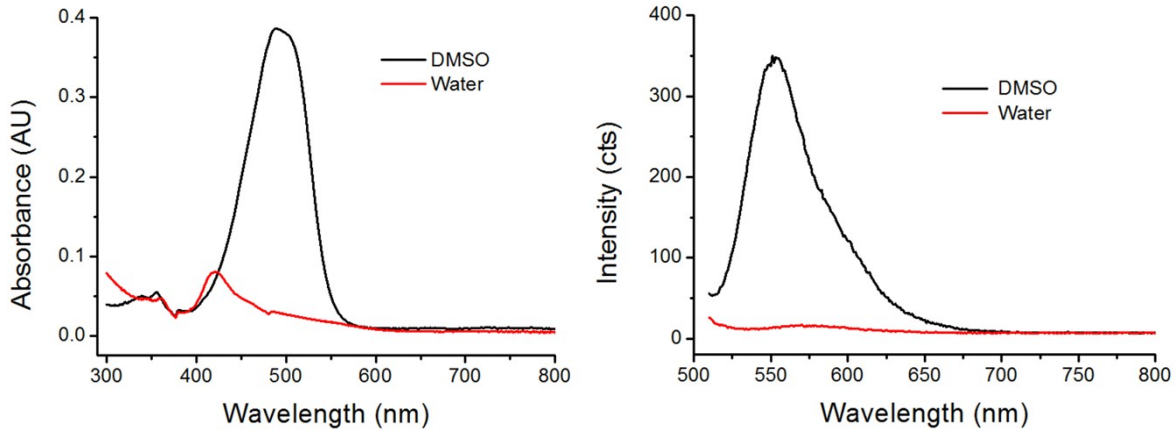

Fig. S7 Absorption (left) and emission (right) spectra of the non-protonated PMI in DMSO and in water.

8. Capture DNA Experiment

The PMI•H$^+$Br$^-$/dsDNA complex was prepared by mixing dsDNA with the specified amount of PMI•H$^+$Br$^-$ solution followed by incubation at room temperature for 5 min. The weight ratio of

PMI•H^+Br^- to dsDNA varied from 0.5 to 5. The complex formation was confirmed by agarose gel electrophoresis. The dsDNA and PMI•H^+Br^-/dsDNA complexes were loaded in the wells of 1.0 wt% agarose gel containing ethidium bromide (EtBr) at a concentration of 0.5 mg mL^{-1}, which was applied to 190 V electrodes in 1 × TBE buffer (pH 9) for 40 min. The dsDNA was visualized by EtBr staining and the gel image was taken under UV.

For energy transfer experiments, different concentrations of PMI•H^+Br^- were added to FAM-labeled DNA solutions. After incubation for 5 min, the fluorescence intensity changes were recorded. For DNA cleavage experiments, 2μL of 18 uM DNA probe was first incubated with 3μL of 400 μM PMI•H^+Br^- at room temperature in PBS buffer solution (20 mM PB, 50 mM NaCl, 1mM EDTA, pH 6.0). After 10 min, different amount of endonuclease Exo III (1-20 U) were added to the sample solution. Then the mixture was incubated at 37°C for 0.5 h. The fluorescence was measured by F-4500 spectrofluorometer (Hitachi Ltd., Japan) (λ_{ex} = 485 nm).

9. Crystal Data and Structure Refinement Results

Table S1 Crystal data and structure refinement results

Compound	PMI•H^+Br^-
Formula	$C_{32}H_{34}BrN_2O_5$
Formula weight	606.52
Temperature (K)	100(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	24.081(5)
b/Å	13.679(3)
c/Å	8.459(2)
α/°	90
β/°	91.87(3)
γ/°	90
V/Å^3	2784.9(10)
Z	4
D_c/g cm^{-3}	1.447

R_{int}	0.0564
R_1 (>2σ)[a]	0.1047
wR_2[b] (all data)	0.3174
Completeness/%	99.8
GOF	1.015

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|.$

[b] $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}.$

Notes and references

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S4 (*a*) T. Ackermann and K. A. Connors, Wiley, New York, 1987; (*b*) P. R. Ashton, R. Ballardini, V. Balzani, M. Belohradsky, M. T. Gandolfi, D. Philp, L. Prodi, F. M. Raymo, M. V. Reddington, N. Spencer, J. F. Stoddart, M. Venturi and D. J. Williams, *J. Am. Chem. Soc.*, 1996, **118**, 4931-4951.