New tetraphenylpyridinium-based luminogens with aggregation-induced emission characteristics

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1  Experimental section

1.1  Materials and instrumentations

2,4,6-Triphenylpyrylium tetrafluoroborate was purchased from Alfa. Aniline was purchased from Sinopharm Chemical Reagent Co. Ltd. p-Phenylenediamine and benzidine were purchased from Aladdin. Solvents, such as dichloromethane, ethanol and ethyl acetate were purchased from Sinopharm Chemical Reagent Co. Ltd. and used without further purification.

1H and 13C NMR spectra were measured on a Mercury Plus 400 MHz NMR spectrometer in DMSO-d$_6$ using tetramethylsilane (TMS; $\delta = 0$ ppm) as internal standard. FT-IR spectra were measured on a Perkin Elmer 16 PC FT-IR spectrophotometer. High-resolution mass spectra (HRMS) were recorded on a Finnigan TSQ 7000 triple-quadrupole mass spectrometer operating in a chemical ionization (CI) mode with methane as carrier gas. Photoluminescence (PL) spectra were recorded on a Perkin-Elmer LS 55 spectrofluorometer. UV absorption spectra were taken on a Varian Cary 100 Bio spectrophotometer.

1.2  Synthesis

Preparation of aggregates

A stock solutions of compounds 1, 2 and 3 in DMSO with concentration of 100 μM were prepared respectively. An aliquot (1 mL) of the stock solution was transferred to 10 mL volumetric flask. After appropriate amount of DMSO was added, water was added dropwise under vigorous stirring to furnish a 10 μM solution with different fractions of water ($f_w = 0$–90 vol%). The absorption and PL measurements of the resultant solutions were performed immediately.

Preparation of 1,2,4,6-tetraphenylpyridinium tetrafluoroborate (1)

2,4,6-Triphenylpyrylium tetrafluoroborate (1.64 g, 4.13 mmol) and anhydrous sodium acetate (1.25 g) were added into a 250 mL of two-necked, round-bottom flask. The flask was evacuated and flushed with dry nitrogen three times. Then, 35 mL of absolute ethanol was injected. The resulting mixture was stirred for 5 min at 60 °C, and then a solution of aniline (0.335 g, 3.60 mmol) in absolute ethanol (3 mL) was added dropwise. After the reaction was refluxed for 24 h, the mixture was then stored at 4 °C overnight, and the precipitate was filtered off. The product was extracted from the solid with dichloromethane, evaporated to dryness under reduced pressure and recrystallized from a mixture of ethyl acetate and dichloromethane [1]. 0.77 g of pure product was obtained as white crystals, yield: 45.23 %. 1H NMR (400 MHz, DMSO-d$_6$): $\delta$ (TMS, ppm) 8.69 (s, 2H), 8.37 (d, 2H), 7.71–7.68 (m,3H), 7.50–7.46 (m, 6H), 7.40–7.37 (m, 6H), 7.21–7.19 (m,3H). 13C NMR (100 MHz, DMSO-d$_6$): $\delta$
Figure S1  $^1$H NMR spectra of compounds 1 (a), 2 (b), and 3 (c) in DMSO-$d_6$.

(TMS, ppm) 156.77, 155.99, 139.53, 133.904, 133.59, 133.01, 130.40, 13.30, 130.21, 130.18, 129.31, 129.15, 128.99, 128.55, 125.59. HRMS (MALDI-TOF): $m/z$: calcd for C$_{29}$H$_{22}$N: 384.1752; found: 384.1765 [M-BF$_4$]$^+$.  

Preparation of compound 2

This compound was synthesized by the same procedure as 1. White solid, yield: 38.14%. $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ (TMS, ppm) 8.43 (s, 4H), 8.39 (d, 4H), 7.72–7.67 (m, 6H), 7.58 (d, 4H), 7.50–7.47 (m, 12H), 7.39–7.37 (m, 12H). $^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta$ (TMS, ppm) 156.74, 155.98, 139.55, 138.72, 133.55, 132.97, 130.19, 129.33, 128.65, 126.81, 125.78. HRMS (MALDI-TOF): $m/z$: calcd for C$_{52}$H$_{38}$N$_2$: 690.3050; found: 689.2697 [M-H-2BF$_4$]$^+$.  

Preparation of compound 3

This compound was synthesized by the same procedure as 1. Yellow solid, yield: 36.44%. $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ (TMS, ppm) 8.43 (s, 4H), 8.27 (d, 4H), 7.67–7.52 (m, 14H), 7.30–7.23 (m, 16H). $^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta$ (TMS, ppm) 156.85, 155.72, 139.55, 138.72, 133.55, 132.97, 130.19, 129.33, 128.65, 126.81, 125.78. HRMS (MALDI-TOF): $m/z$: calcd for C$_{52}$H$_{38}$N$_2$: 853.3377; found: 853.3357 [M-BF$_4$]$^+$.  

Figure S2 $^{13}$C NMR spectra of compounds 1 (a), 2 (b), and 3 (c) in DMSO-$d_6$. 

(a)

(b)

(c)
Figure S3  High resolution mass spectra of compounds 1 (a), 2 (b), and 3 (c).
Figure S4  UV-vis spectra of compounds 1, 2 and 3 in DMSO. Concentration: 10 µM.

Figure S5  PL spectra of compound 1 in the DMSO/water mixtures with different fractions of water. Concentration: 10 µM; excitation wavelength: 309 nm.

Figure S6  PL spectra of compound 3 in the DMSO/water mixtures with different fractions of water. Concentration: 10 µM; excitation wavelength: 317 nm.

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