Supporting Information

N-Monoalkylated 1,4-Diketo-3,6-diphenylpyrrolo[3,4-c]pyrroles as Effective One- and Two-photon Fluorescence Chemosensors for Fluoride Anion[†]

Chao Yang, Meng Zheng, Yiping Li, Baoliang Zhang, Jinfeng Li, Lingyu Bu, Wei Liu, Mingxiao Sun, Haichang Zhang, Yong Tao, Shanfeng Xue and Wenjun Yang*

1. Experimental section

1.1 Materials.

3,6-Dip-tolylpyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione and 3,6-bis(4-chlorophenyl)pyrrolo[3,4-c]pyrrole-1,4(2H, 5H)-dione were purchased from Guangzhou Yulong Chemical Ltd., China. 3,6-Bis(4-bromophenyl)-pyrrolo[3,4-c] pyrrole-1,4(2H,5H)-dione was from previous work¹. DMF was distillated over calcium hydride before use. Other reagents and solvents were analytical grade and used as received, unless otherwise claimed.

1.2 Synthesis of mDPP-X.

3,6-Bis(4-bromophenyl)-2-octylpyrrolo[3,4-c]pyrrole-1,4(2H, 5H)-dione (mDPP-Br). To a stirred suspension of 3,6-bis(4-bromophenyl)pyrrolo-[3,4-c]pyrrole-1,4(2H,5H)-dione (1.14 g, 2.6 mmol) in DMF (30 mL) at room temperature, potassium *tert*-butoxide (0.81 g, 7.1 mmol) was added under N₂. The mixture turned into purple and was stirred for 30 min. 1-Bromooctane (0.83 g, 4.3 mmol) was gradually added and the resultant reddish mixture was stirred for 6 h at room temperature. The mixture was poured into 400 mL of water and stirred for 1 h. The crude product was obtained by filtration and then further purified by flash column chromatography using DCM/ethyl acetate = 5/1 as the eluent. Yield: 0.65 g (51%). ¹H NMR (500 MHz, CDCl₃), δ (ppm): 10.04 (s, 1H), 8.15-8.16 (d, 2H), 7.64-7.69 (d, 4H), 7.55-7.57 (d, 2H), 3.75-3.78 (t, 2H), 1.45-1.60 (t, 2H), 1.21-1.61 (m, 10H), 0.80-0.90 (m, 3H). ¹³C NMR (125 MHz, CDCl₃): δ (ppm) 163.5, 162.1, 147.0, 144.1, 132.1, 131.9, 130.3, 129.4, 126.7, 126.5, 126.3, 126.0, 111.2, 109.6, 53.4, 42.5, 31.7, 29.5, 29.2, 26.8, 22.6, 14.1. Anal. Calcd (%) for C₂₆H₂₆Br₂N₂O₂: C, 55.93; H, 4.69; Br, 28.62; N, 5.02; O, 5.73. Found: C, 55.86; H, 4.71; N, 5.06.

3,6-Bis(4-chlorophenyl)-2-octylpyrrolo[3,4-*c***]pyrrole-1,4-(2H, 5H)-dione (mDPP-Cl).** To a stirred suspension of 3,6-bis(4-chlorophenyl)pyrrolo-[3,4-*c*]**pyrrole-1,4(**2H,5H)-dione (5.0 g, 11.2 mmol) in DMF (120 mL) at room temperature, potassium *tert*-butoxide (3.45 g, 30.24 mmol) was added under N₂. After stirring for 30 min, 1-bromooctane (3.2 mL, 18.5 mmol) was gradually added and the resultant reddish mixture was stirred for 10 h at room temperature. The mixture was poured into 600 mL of water and then stirred for 1 h. The solid obtained by filtration was purified by a flash column chromatography using DCM/ethyl acetate = 6/1 as the eluent. Yield: 3.11 g (47.3%). ¹H NMR (500 MHz, CDCl₃), δ (ppm) 9.31 (s, 1H), 8.12-8.26 (d, 2H), 7.77-7.79 (d, 2H), 7.53-7.55 (d, 2H), 7.47-7.49 (d, 2H), 3.813 (t, 2H), 1.50 (t, 2H), 1.22-1.24 (m, 10H), 0.872 (m, 3H). ¹³C NMR (125MHz, CDCl₃): δ (ppm) 163.6, 162.1, 146.9, 144.0, 137.9, 137.5, 130.2, 129.4, 129.1, 128.9, 126.1, 126.0, 111.2, 109.5, 42.5, 31.7, 29.5, 29.2, 29.0, 26.8, 22.6, 14.1. Anal. Calcd (%) for C₂₆H₂₆Cl₂N₂O₂: C, 66.53; H, 5.58; Cl, 15.11; N, 5.97; O, 6.82. Found: C, 66.61; H, 5.53; N, 5.95.

3,6-Bis(4-methylphenyl)-2-octylpyrrolo[3,4-*c***]pyrrole-1,4(2H, 5H)-dione** (**mDPP-Me**). To a stirred suspension of 3,6-bis(4-methylphenyl)pyrrolo[3,4-*c*]**pyrrole-1,4(2H,5H)-dione** (0.82 g, 2.6 mmol) in DMF (30 mL), potassium *tert*-butoxide (0.8 g, 7.1 mmol) was added at room temperature under N₂. The resultant mixture was stirred for 30 min and 1-bromooctane (0.83 g, 4.3 mmol) was added slowly. After stirring for 10 h at room temperature, the mixture was poured into 400 mL of water and stirred for 1 h. The solid obtained by filtration was purified by flash column chromatography using DCM/ethyl acetate = 6/1 as the eluent. Yield: 0.65 g (59.1%). ¹H NMR (500 MHz, CDCl₃), δ (ppm): 9.43 (s, 1H), 8.21-8.23 (d, 2H), 7.71-7.73 (d, 2H), 7.33-7.35 (d, 2H), 7.23-7.31 (d, 2H), 3.83 (t, 2H), 2.43-2.45 (s, 6H), 1.61-1.64 (t, 2H), 1.19-1.24 (m, 10H), 0.82-0.85 (m, 3H). ¹³C NMR (125 MHz, CDCl₃): δ (ppm) 163.7, 162.7, 147.8, 144.9, 142.6, 141.6, 129.8, 129.1, 129.5, 128.9, 128.1, 125.5, 125.2, 110.6, 109.1, 42.2, 31.7, 29.5, 29.1, 26.8, 22.6, 21.9, 14.1. Anal. Calcd (%) for C₂₈H₃₂N₂O₂: C, 78.47; H, 7.53; N, 6.54; O, 7.47. Found: C, 78.53; H, 7.51; N, 6.57.

1.3 Measurement.

The NMR spectra were recorded on a Bruker-AC500 (500 MHz) spectrometer in $CDCl_3$ with teramethylsilame (TMS) as the internal standard. The elemental analysis was performed on Perkin–Elmer 2400.

UV-vis absorption spectra were recorded on a Hitachi U-4100 spectrophotometer. Fluorescence measurements were carried out with Hitachi F-4600 spectrophotometer, and the peak wavelength of the lowest energy absorption band was used as the excitation wavelength. The fluorescence quantum yield (Φ) was determined in THF at room temperature using Rhodamine B in methanol as the reference according to the dilute solution method.¹ The uncertainty for measured UV or PL is < 2%. The fluorometric cuvette with $1.0 \times 1.0 \text{ cm}^2$ cross section and four optically clear windows was used.

The two-photon absorption (2PA) cross-sections (δ) were measured with the two-photon-induced fluorescence method by using femtosecond laser pulses as described before by us and others.^{2,3} The excitation light source was a mode-locked Ti:sapphire fs laser (Spectra-Physics, Tsunami 3941, 700-910 nm, 80 MHz, <120 fs) pumped by a compact cw prolite diode laser (Spectra-physics, Millennia Pro 5S). The fluorescence signal was recorded by a spectrofluorometer (Ocean Optics, USB2000). Samples were dissolved in THF at the concentrations of 1.0×10^{-5} M and the two-photon induced fluorescence intensity was measured at 710–800 nm by using Rhodamine B (1.0×10^{-5} M in methanol) as the reference.⁴ The intensities of the two-photon induced fluorescence spectra of the reference and sample under the same measurement conditions were determined and compared. The two-photon absorption cross section of sample (δ_s) was calculated by using the equation: $\delta_s = [(S_s \Phi_r n_r^2 c_r)/(S_r \Phi_s n_s^2 c_s)]\delta_r$, where the subscripts s and r stood for the sample and reference molecules respectively. S was the integral area of the two-photon excitation fluorescence; Φ was the fluorescence quantum yield (assuming that both in two photon and one photon excitation, the Φ remains unchanged), n was the refractive indices of the solvents for the sample and reference, and *c* was the number density of the molecules in solution. δ_r was the TPA cross section of the reference molecule. The whole experimental uncertainty in δ is about 15%.

References

(1) J. N. Demas, G. A. Crosby, J. Phys. Chem., 1971, 75, 991.

- (2) (a) E. Q. Guo, P. H. Ren, Y. L. Zhang, H. C. Zhang, W. J. Yang, *Chem. Commun.*, 2009, 5859; (b) B. Zhang, H. Zhang, X. Li,
 W. Li, P. Sun, W. Yang, *J. Polym. Sci. Part A: Polym. Chem.*, 2011, 49, 3048.
- (3) (a) M. Rumi, J. E. Ehrlich, A. A. Heikal, J. W. Perry, S. Barlow, Z. Hu, D. McCord-Maughon, T. C. Parker, H. Rockel, S. Thayumanavan, S. R. Marder, D. Beljonne, L. J Brédas, *J. Am. Chem. Soc.*, 2000, **122**, 9500; (b) B. R. Cho, K. H. Son, S. H. Lee, Y. S. Song, Y. K. Lee, S. J. Jeon, J. H. Choi, H. Lee and M. Cho, *J. Am. Chem. Soc.*, 2001, **123**, 10039.

(4) C. Xu, W. W. Webb, J. Opt. Soc. Am. B, 1996, 13, 481.

2. Other supporting figures



Figure S1. Normalized one-photon absorption spectra of **mDPP-X** in THF upon adding different equiv of TBAF.



Figure S2. Normalized one-photon excited fluorescence spectra of **mDPP-X** in THF upon adding different equiv of TBAF.



Fig. S3 Two-photon excitation fluorescence (2PEF) spectra of mDPP-X.





Figure S4. Normalized two-photon excited fluorescence spectra of **mDPP-X** in THF upon adding different equiv of TBAF.