Aggregation induced emission in the rotatable molecules: The essential role of molecular interaction

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Synthesis and characterizations

Synthesis. The three compounds, **dye1**, **dye2** and **dye3**, have been prepared according to synthetic routes shown in Scheme 1. The experimental details are introduced as follows:

Synthesis of 4-Diethylaminobenzaldehyde (a1): 4-Diethylaminobenzaldehyde was prepared referring the literature [21].

Synthesis of 4-(1, 4, 7, 10 – tetraoxa-13- aza cyclopentadecyl) benzaldehyde (a2): 4-(1, 4, 7, 10-tetraoxa-13-aza cyclopentadecyl) benzaldehyde was prepared referring the literature [22].

Synthesis of 4-(1, 4, 7, 10, 13 – tetraoxa-16- aza cyclopentadecyl) benzaldehyde (a3): 4-(1, 4, 7, 10, 13 – tetraoxa-16- aza cyclopentadecyl) benzaldehyde was prepared referring the literature [23].

Preparation of dye1: a1 (1.25g, 7mmol) was dissolved in 50 mL of ethanol. Hydrazine hydrate (0.2 g, 3.4 mmol; 85%) was then added dropwise with vigorous stirring at room temperature. The stirred mixture was allowed to stand at room temperature overnight, and the resulting precipitation was filtered and recrystallization with ethanol to give 0.78g of the yellow crystal. Yield: 66 %. *m/z* 351.23(M^++1). ^{1}H-NMR (DMSO-d_6, 400 MHz, TMS): δ 8.45 (s, 2H) 7.59-7.61 (d, 4H, J = 8.4 Hz) 6.70-6.72 (d, 4H, J = 8.4 Hz) 3.38-3.43 (q, 8H, J = 3.4 Hz) 1.10-1.14 (t, 12H, J = 3.4 Hz). ^{13}C-NMR ($CDCl_3$, 100 MHz, TMS): δ 160.49, 149.64, 130.12, 120.94, 111.13, 44.46, 12.61. IR (KBr, cm^{-1}) 2971, 2929, 2889, 1598, 1519, 1468, 1401, 1355, 1266, 1179, 1197, 1152, 1075, 1005, 963, 818.

Preparation of dye2: dye2 was prepared according to a similar procedure to **dye1**, using a2 (2.26 g, 7 mmol) instead of a1, to produce the 1.43 g of yellow crystal. Yield of 65%. *m/z* 643.37 (M^++1). ^{1}H-NMR (DMSO-d_6, 400 MHz, TMS): δ 8.47 (s, 2H) 7.60-7.63 (d, 4H, J = 8.8 Hz) 6.71-6.73 (d, 4H, J = 8.8 Hz) 3.65-3.68 (t, 8H, J = 5.8 Hz) 3.56-3.59 (t, 24H, J = 6.4 Hz) 3.51 (s, 8H). ^{13}C-NMR ($CDCl_3$, 100 MHz, TMS): δ 160.57, 149.64, 130.02, 122.06, 111.32, 70.32, 70.25, 70.10, 68.34, 52.68. IR (KBr, cm^{-1}) 2941, 2889, 2869, 1605, 1520, 1471, 1378, 1354, 1323, 1290, 1227, 1188, 1121, 1090, 1058, 976, 939, 818.

Preparation of dye3: dye3 was prepared according to a similar procedure to **dye1**, using a3 (2.57 g, 7 mmol) instead of a1, to produce the 1.44 g of yellow crystal. Yield: 58%. m/z 731.45 (M^++1). ^{1}H-NMR (DMSO-d_6, 400 MHz, TMS): δ 8.47 (s, 2H) 7.60-7.62 (d, 4H, J = 8.4 Hz) 6.76-6.74 (d, 4H, J = 8.4 Hz) 3.54-3.61 (s, 16H) 3.54-3.56 (t, 32H, J = 3.0 Hz). ^{13}C-NMR ($CDCl_3$, 100 MHz, TMS): δ 160.32, 150.13, 130.28, 121.53, 111.41, 70.81, 70.34, 68.48, 68.30, 51.30. IR (cm^{-1}) 2931, 2886, 2864, 1605, 1519, 1385, 1350, 1273, 1189, 1116, 1057, 951, 818.

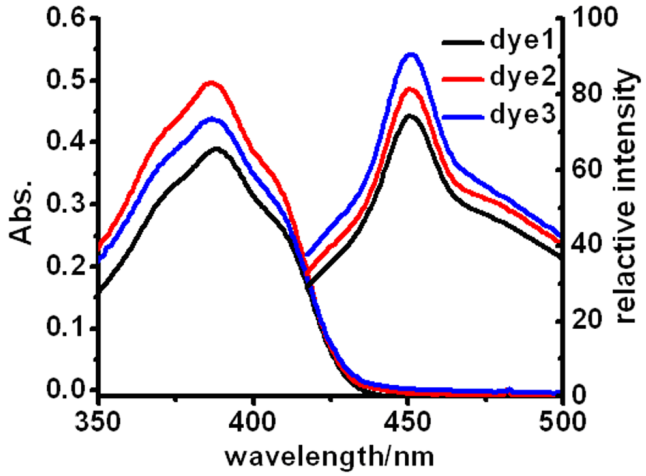

Fig. S1 The absorption and fluorescence spectra of **dye1**, **dye2** and **dye3** in the dilute THF solution

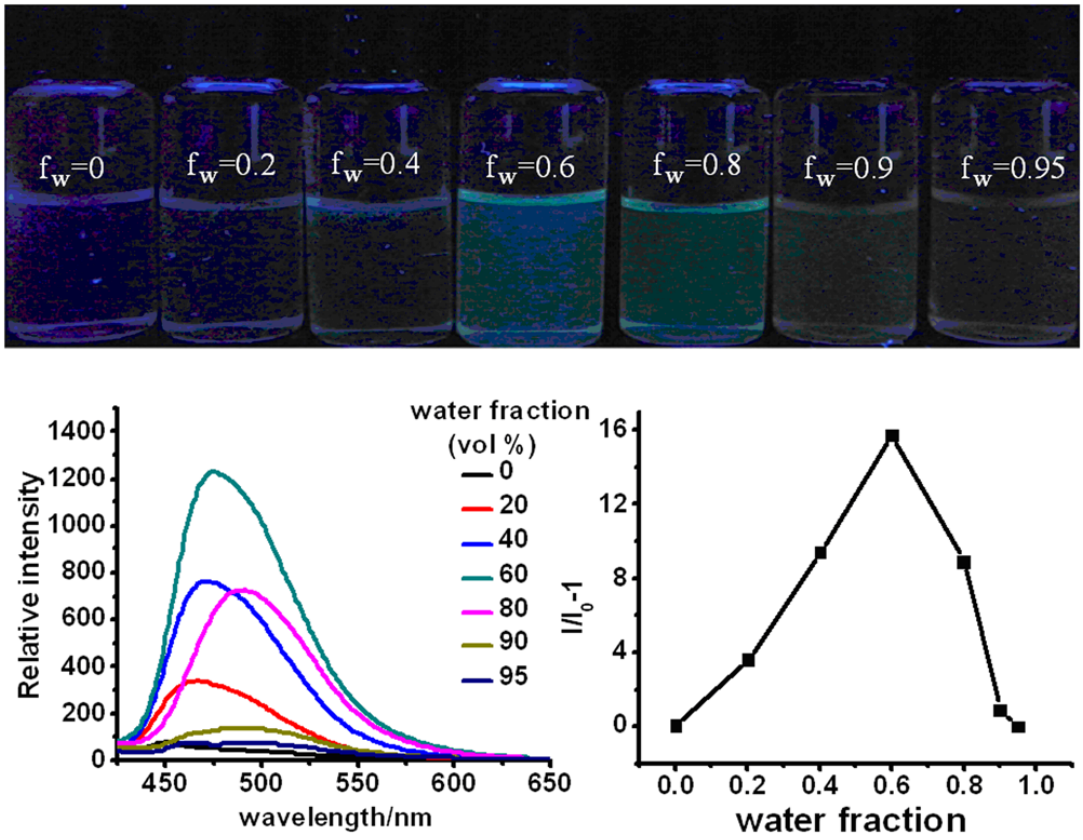

Fig. S2 (A) Photographs of **dye1** in THF/H_2O mixtures with different water fractions (f_w) taken under UV illumination. (B) Emission spectra of **dye1** in THF/H_2O mixtures. (C) Plot of (I/I_0 - 1) values versus the compositions of the aqueous mixtures. I_0=emission intensity in pure THF solution. Solution concentration: 10 μM

Table S1. Excitation energies (E), oscillator strengths (f), corresponding wavelengths (λ_{abs}) and major contributors for **dye1**, **dye2** and **dye3**.

	E(eV)	f	λ_{abs}(nm)	composition (*C*)	Character
dye1	3.2059	1.7929	387	94(H)→95(L) (0.64663)	π → π*
dye2	3.1910	1.8754	389	173(H) →174(L) (0.64843)	π → π*
dye3	3.1748	1.8608	391	197(H)→198(L) (0.64615)	π → π*