Reversable piezofluorochromic nature and mechanism of Aggregation-Induced Emission-Active compounds based on simple modification

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Experimental section

Materials and Instrumentations

All chemicals were available commercially. DMF was HPLC grade from BODI Organic Company and was used as received. All the chemicals were used directly without further purification. The NMR spectra were recorded on a 400 MHz NMR instrument. Chemical shifts were reported in parts per million (ppm) relative to internal TMS (0 ppm) and coupling constants in hertz. Splitting patterns were described as singlet (s), doublet (d), triplet (t) or multiplet (m). IR spectra were recorded with a Nicolet FT-IR NEXUS 870 spectrometer (KBr discs). UV-vis absorption spectra were recorded on a UV-3100 spectrophotometer. The mass spectra were obtained on a LTQ Orbitrap XL mass spectrometer (2 and 4) and a SATUKN2200 gas chromatography-mass spectrometer (GC/MS) (3). The scanning electron microscopy (SEM) was performed using the Hitachi S-4800 scanning electron microscope. Fluorescence measurements were carried out using an Edinburgh FLS920 fluorescence spectrometer equipped with a 450W Xe-lamp and a time-correlated single-photon counting (TCSPC) card. The X-ray diffraction measurements of single crystals were performed on a Bruker Smart 1000 CCD area detector using graphite monochromated MoKα radiation (λ = 0.71069 Å). Intensity data were collected in the variable ω-scan mode. The structures were solved by direct methods and difference Fourier syntheses. The non-hydrogen atoms were refined anisotropically and hydrogen atoms were introduced geometrically. The theoretical calculations of 1-4 were performed with the density functional of B3LYP/6-31G(d). The WXRD measurements were carried out using an MXP18AHF
X-ray diffractometer. All the measurements above were all carried out in the room temperature.

**Synthesis**

**Scheme S1.** Synthesized routes to 1, 2, 3 and 4.

*Synthesized of 4-Diphenylamino-benzaldehyde (1).* The intermediate 1 was synthesized efficiently according to the literature.

*Synthesized of 2-(4-Diphenylamino-benzylidene)-malononitrile (2).* 4-Diphenylamino-benzaldehyde (0.5 g, 1.8 mmol) was added to the ethanol solution (30 mL) of malononitrile (0.1 g, 1.8 mmol). The mixture was stirred at 60 °C and the reaction was monitored by TLC. After 2 h the mixture was completely reacted and cooled down to room temperature. Orange powder (0.39 g) was obtained through vacuum filtration, yield: 69 %. $^1$H-NMR (400 MHz, DMSO-D$_6$), δ (ppm): 8.21 (s, 1H), 7.83-7.81 (d, $J = 8.0$ Hz, 2H), 7.46-7.43 (t, $J = 6.0$ Hz, 4H), 7.30-7.23 (m, 6H), 6.85-6.83 (d, $J = 8.0$ Hz, 2H); $^{13}$C-NMR (100 MHz, DMSO-D$_6$), δ (ppm): 159.29, 152.89, 144.68, 133.07, 130.12, 126.76, 126.23, 122.57, 117.39, 115.37, 114.42, 73.69. IR (KBr, cm$^{-1}$): 2967, 1602, 1574, 1524, 1453. MS (MALDI-TOF): m/z 321.127 [(M-1)$^+$, calcd 319.872].

*Synthesized of 1-Ethoxy-4-iodo-benzene (a).* Sodium hydroxide (24.0 g, 0.6 mol) and 4-Iodo-phenol (120.0 g, 0.54 mol) were crushed together in batches with a pestle and mortar. And then bromoethane (300 mL) was added to this white power. To this solution, cesium hydroxide (10 g)
in 20 mL of DMF and 3 drops of 18-crow-6 was added and stirred for 1 h at room temperature. Then the reaction mixture was heated at 60 °C for 78 h. The mixture was concentrated and cooled to RT after the reaction was completed by monitoring with TLC. Much water was added to it and the mixture was extracted with dichloromethane (100 mL) three times. The organic extracts were dried over MgSO₄. After removing solvents under reduced pressure, red oily liquid was obtained (128.4 g, yield: 94.9 %).

Synthesized of Bis-(4-ethoxy-phenyl)-phenyl-amine (b). Aniline (5.0 g, 54 mmol) and 1-Ethoxy-4-iodo-benzene (46.0 g, 185 mmol) were added to 1, 2-Dichlorobenzene (200 mL) in a three-neck flask. Potash (17.94 g, 130 mmol) and copper powder (8.34 g, 130 mmol) were slowly added to the mixture after stirred for a little moment in the atmosphere of nitrogen. Three drops of 18-crown-6 were added to the mixture. The mixture was reacted at 180 °C for 12 h. The mixture was cooled to RT after the reaction complete. The solvent was removed under reduced pressure and the mixture was purified by chromatography on silica gel using petroleum ether/ethyl acetate (50:1, v/v) as eluent, and white crystals was given, 7.8 g, yield: 43.6%. ¹H-NMR (400 MHz, (CD₃)₂CO), δ (ppm): δ (ppm): 7.18-7.14 (t, J = 7.6 Hz, 2H), 7.02-7.00 (d, J = 8.4 Hz, 4H), 6.86-6.71 (m, 7H), 4.04-3.99 (m, 4H), 1.37-1.34 (t, J = 7.0 Hz, 6H).

Synthesized of 4-[Bis-(4-ethoxy-phenyl)-methyl]-benzaldehyde (3). POCl₃ (2.3 mL) was added dropwise to fresh distilled DMF (2.8 mL) which was stirred in flask (150 mL) using ice water bath cooling. After 30 minutes, the solution became sticky and was stirred a little longer to yield a reddish salt resembling ice. Then the salt was combined with a portion of b (5.0 g, dissolved in 15 mL chloroform) to yield a reddish solution. Then the reaction mixture was heated at 65 °C for 10 h. The reaction was monitored by TLC. After the reaction was completed, it was concentrated. The black mixture was dissolved in dichloromethane and then poured into much water. Na₂CO₃ solution (40 %) was added to adjust the pH of the mixture to 7-8. Then extract it three times with dichloromethane and the organic extracts were dried over MgSO₄. After removing solvents under reduced pressure, the mixture was purified by chromatography on silica gel using petroleum ether/ethyl acetate (40:1, v/v) as eluent, giving yellow-green solid 5.21g, yield: 96.15%. ¹H-NMR (400 MHz, (CD₃)₂CO), δ (ppm): 9.70 (s, 1H), 7.66-7.63 (d, J = 8.4 Hz, 2H), 7.20-7.18 (d, J = 8.8 Hz, 4H), 6.99-6.96 (d, J = 8.4 Hz, 4H), 6.69-6.66 (d, J = 8.8 Hz, 2H), 4.05-4.00 (m, 4H), 1.35-1.31 (t, J = 7.0 Hz, 6H). ¹³C-NMR (100 MHz, DMSO-D6), δ (ppm): 190.11, 156.50, 153.70,
Synthesized of 2-[4-{Bis-(4-ethoxy-phenyl)-amino]-benzylidene]-malononitrile (4). 4-[Bis-(4-ethoxyphenyl)-amino]-benzaldehyde (0.65 g, 1.8 mmol) was added to ethanol solution (30 mL) of malononitrile (0.1 g, 1.8 mmol). The mixture was stirred at 60 °C and the reaction was monitored by TLC. After 3 h the mixture was completely reacted and cooled down to room temperature. The crude product was purified by column chromatography on silica, eluting with Petrol ether-ethyl acetate (20:1, v/v) to yield 4 as orange block solid (0.47 g), yield: 64 %. $^1$H-NMR (400 MHz, DMSO-D6), δ (ppm): 8.13-8.12 (d, $J = 3.6$ Hz, 1H), 7.78-7.76 (d, $J = 8.4$ Hz, 2H), 7.22-7.20 (m, 4H), 6.99-6.98 (d, $J = 6.8$ Hz, 4H), 6.88-6.66 (d, $J = 8.4$ Hz, 2H), 4.05-4.01 (m, 4H), 1.35-1.32 (t, $J = 7.0$ Hz, 6H); $^{13}$C-NMR (100 MHz, DMSO-D6), δ (ppm): 159.01, 156.91, 153.84, 137.05, 133.22, 128.40, 121.26, 115.72, 115.64, 115.29, 114.73, 71.92, 63.27, 14.59. IR (KBr, cm$^{-1}$): 2972, 1627, 1573, 1519, 1431, 1379, 1242, 1057. MS (MALDI-TOF): m/z 408.093 [(M+1)$^+$, calcd 409.179].

Fig. S1 $^1$H-NMR spectrum of 2.
Fig. S2 $^{13}$C-NMR spectrum of 2.

Fig. S3 MS spectrum of 2.
Fig. S4 $^1$H-NMR spectrum of 3.

Fig. S5 $^{13}$C-NMR spectrum of 3.
Fig. S6 MS spectrum of 3.

Fig. S7 1H-NMR spectrum of 4.
Fig. S8 $^{13}$C-NMR spectrum of 4.

Fig. S9 MS spectrum of 4.

References

Fig. S10 PL spectra of the compounds 1, 3 and 4 in DMF/water mixtures with different water fractions (excitation wavelength: 365 nm). The top and bottom insets depict the change in the PL peak intensity and the emission photos of compounds 1, 3, 4 in mixtures of different water fraction under 365 nm irradiation, respectively.
**Fig. S11** UV-vis absorption spectra of 1, 3 and 4 in DMF/H$_2$O mixture with different water fractions.

**Fig. S12** (a) PL spectra and (b) photographs of 1 in varying solutions from low polarity to high polarity.

**Fig. S13** Energy level and electron density distribution of frontier orbitals of compounds 1-4.
**Fig. S14** Photographs of 1, 3 and 4 taken at RT under UV-light (365 nm) after grinding and fuming/annealing.

**Fig. S15** The normalized PL intensity curves and maximum PL intensity change of compounds 1, 3 upon repeated fuming and grinding. 4: the PL intensity change of 4 upon as-synthesized and after grinding.
**Fig. S16** The normalized PL intensity curves (1a, 2a and 3a) and maximum PL intensity change (1b, 2b, 3b) of compounds 1, 2 and 3 upon repeated annealing and grinding.
**Fig. S17** SEM of the as-synthesized sample (a) and ground sample (b) of 4.

**Fig. S18** WAXD patterns of compounds 1, 3 and 4: (a) as-synthesized sample, (b) ground sample, (c) fuming with DCM vapor for 5 minutes, (d) annealing at 80°C for 10 minutes.
**Fig. S19** Molecular packing of 1 in single crystals with C-H…π (2.949 Å), C-H…O (2.514 Å) hydrogen bonds indicated.