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Electronic Supplementary Information (ESI)

Locking the phenyl rings of tetraphenylethene step by step: Understanding the mechanism of aggregation-induced emission

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Experimental section

Materials and Instrumentations

Tetrahydrofuran (THF), ethylene glycol dimethyl ether (DME) were purified by distillation over sodium/benzophenone under nitrogen before use. Other reagents were commercially obtained from Beijing and used as received without additional purification.

^{1}H and ^{13}C NMR spectra were recorded using a Bruker AV 400 Spectrometer at 400 and 100 MHz in THF-d_6 solutions respectively, using tetramethylsilane (TMS; δ

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= 0) as internal reference. Mass spectra was recorded on a triple quadrupole mass spectrometer (finnigan TSQ7000). UV-vis absorption spectra were recorded on a TU-1901. Infra-red (IR) spectra were obtained using KBr pellets on a Nicolet Fourier spectrofluorometer. Photoluminescence (PL) spectra were recorded on a Perkin-Elmer LS 55 spectrofluorometer. Quantum yields of all samples were recorded on horiba fluoromax 4 with a calibrated intergrating sphere system. Thermal transitions were investigated by differential scanning calorimetry (DSC) using a Mettler DSC 1 instrument at a heating rate of 10 K/min. Powder X-Ray diffraction (XRD) patterns were performed on a X'Pert PRO MPD diffractometer with Cu Kα radiation (λ = 1.5418 Å) at 25 ℃ (scan range: 4.5-50°). Single crystal X-ray diffraction intensity data were collected on a Bruker Smart APEXII CCD diffractometer using graphite monochromated Mo Kα radiation (λ=0.71070 Å). Single crystal of 1OTPE was grown from the solvent mixed by dichloroethane and petroleum ether, single crystal of 2OTPE was grown from the solvent mixed by tetrahydrofuran and petroleum ether. The structures were solved by direct methods and refined with the full-matrix least-squares technique based on F2 using the SHELXL program.All photographs were recorded on a FinePix S7000 digital camera.

Synthesis

9-(diphenylmethylene)-9H-xanthene(1OTPE) and 9,9'-bixanthenylidene(2OTPE) were prepared according to Scheme S1 following the synthetic procedures given in the literature [1] , the reaction was carried out under a dry nitrogen atmosphere using Schlenk technique, which was a typical cross McMurry coupling reaction.

Their characterization data are given below.

9-(diphenylmethylene)-9H-xanthene(1OTPE). Yield 30%. M.p. 197-199 ℃. ^{1}H NMR (400 MHz, THF-d_6): 7.31-7.29 (t, 4H), 7.25-7.22 (t , 4H), 7.18-7.13 (t , 2H), 7.11-7.01 (m, 4H), 6.92-6.90 (d, 2H), 6.67-6.63 (m, 2H). ^{13}C NMR (100 MHz, THF-d_6): 151.9, 141.4, 137.1, 127.4, 127.0, 126.4, 125.9, 124.6, 123.4, 122.6, 120.1, 114.1. MS (CI): m/e 346.4 (M+, calcd. 346.4).

IR (KBr, cm^{-1}): ν = 3437 (s), 1602 (s), 1446 (s), 1251 (s), 1134 (m), 745 (s).

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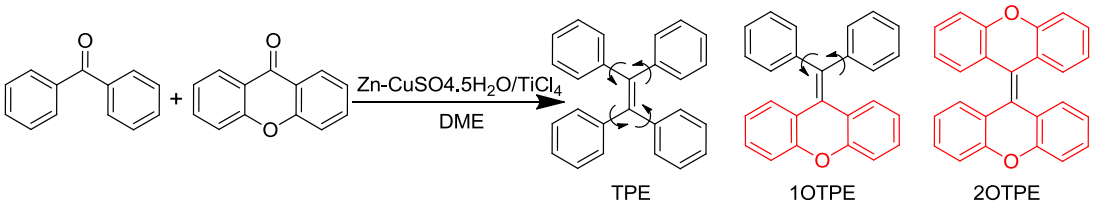
9,9'-bixanthenylidene(2OTPE). Yield 35%. M.p. 300-302 ℃. ^{1}H NMR (400 MHz, THF-d_6): 7.31-7.25 (m, 8H), 7.16-7.14 (d , 4H), 6.93-6.89 (m , 4H). ^{13}C NMR (100 MHz, THF-d_6): 153.7, 126.4, 126.0, 123.0, 120.4, 119.5, 114.9. MS (CI): m/e 360.3 (M+, calcd. 360.4).

IR (KBr, cm^{-1}): ν = 3443 (s), 1632 (m), 1437 (m), 1257 (s), 1206 (m), 766 (s).



Scheme S1. Synthesis of three luminogens.

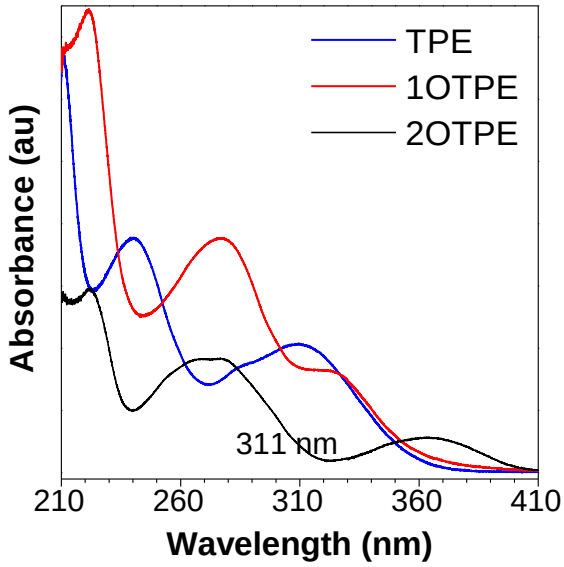


Figure S1. UV spectra of TPE, 1OTPE and 2OTPE in THF. Concentration: 10 μM.

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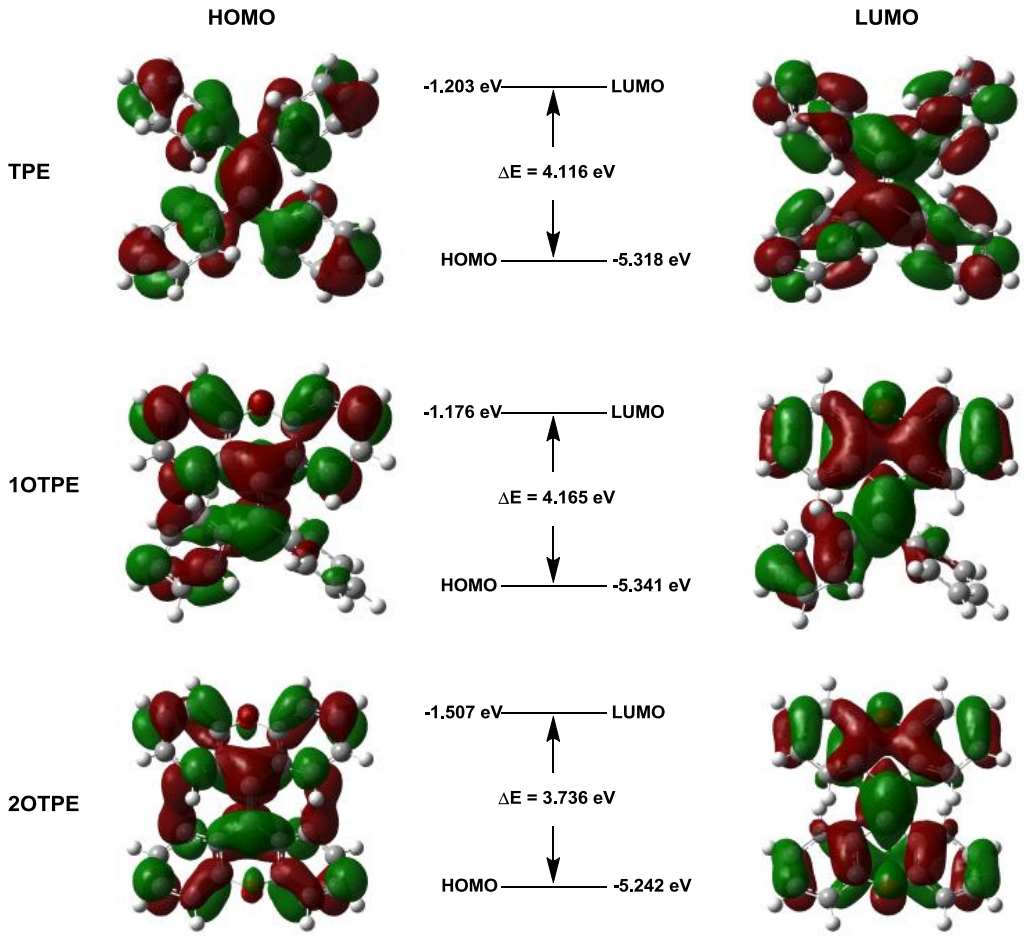

Figure. S2 Molecular orbital amplitude plots of HOMO and LUMO energy levels of TPE, 1OTPE and 2OTPE. (Caculated by Gaussian 09 through B3LYP/6-31g(d) method)

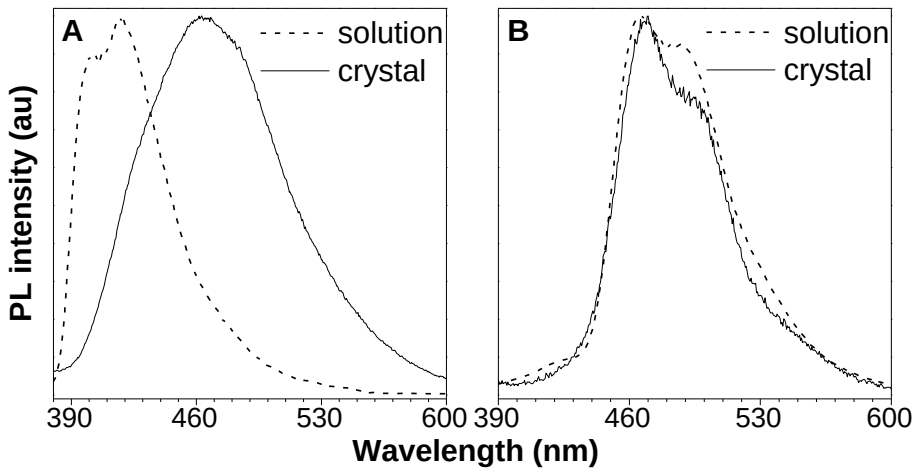

Figure S3. PL spectra of (A) 1OTPE and (B) 2OTPE in solution and crystals.

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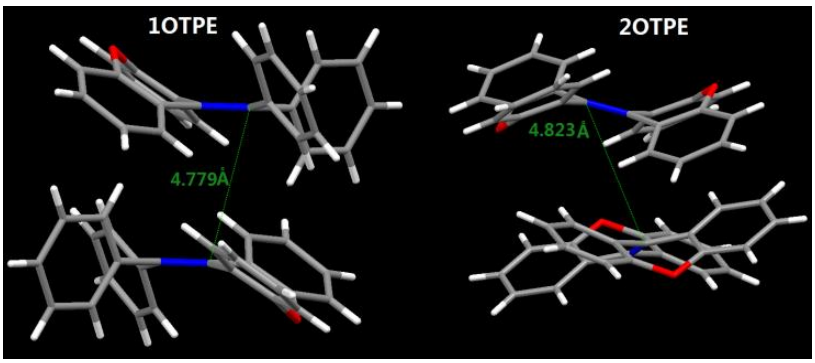

Figure S4. View of molecule conformation and molecule distance in crystals of 1OTPE and 2OTPE.

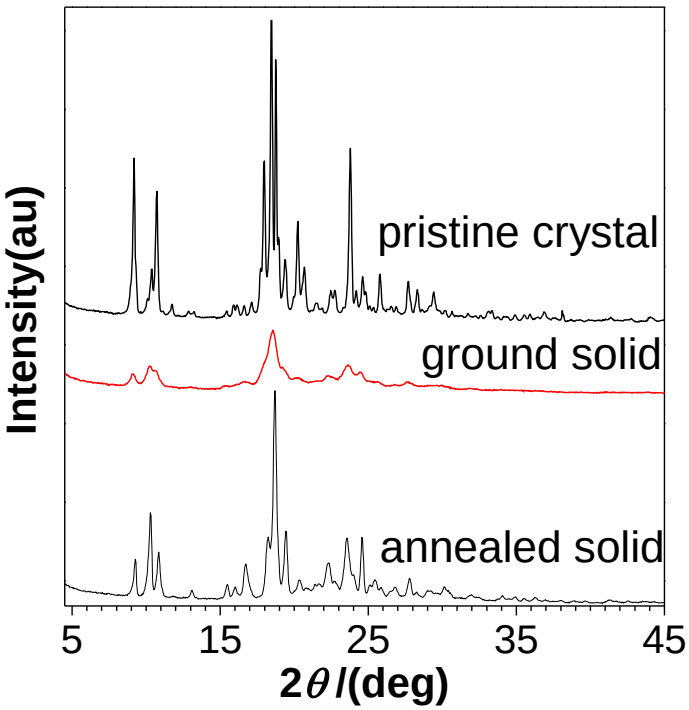

Figure S5. Powder XRD patterns of 1OTPE solids: pristine crystal, ground solid, the annealed solid. Annealed condition: 170 °C, 2 hours.

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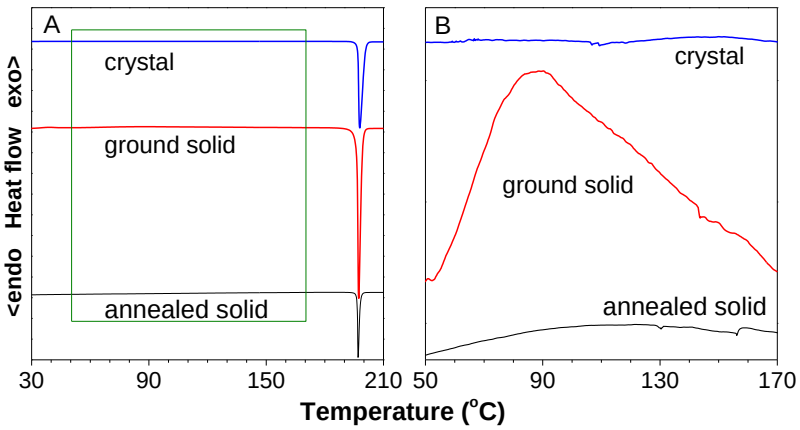

Figure S6. (A) DSC thermograms of crystal, ground and annealed solid of 1OTPE and (B) selected area was enlarged for easy comparison.

Table 1. Summary of crystal data and intensity collection parameters for 1OTPE and 2OTPE.

	1OTPE	**2OTPE**
Empirical formula	$C_{26}H_{18}O$	$C_{26}H_{16}O_2$
Formula weight	346.40	360.39
Crystal size, mm	0.57 x 0.43 x 0.40	0.26 x 0.23 x 0.20
Crystal system	Monoclinic	Monoclinic
space group	P2(1)/c	C2/c
a, Å	11.9746(15)	14.829(10)
b, Å	9.4799(12)	12.847(8)
c, Å	19.8636(19)	9.436(6)
a, deg	90	90
β, deg	125.669(5)	95.261(11)
γ, deg	90	90
V, $Å^3$	1831.9(4)	1790(2)
Z	4	4
Calculated density, Mg/m^3	1.256	1.337

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$F(000)$	728	752
Temperature, K	150(2)	150(2)
Wavelength, Å	0.71073	0.71073
μ(Mo Ka), mm^{-1}	0.075	0.084
$2\theta_{max}$, deg(Completeness)	55.24(98.6 %)	50.48(99.9 %)
no. of collected reflections	10566	4433
no. of unique ref.(R_{int})	4208(0.0354)	1617(0.0529)
Data/restraints/parameters	4208/0/244	1617/0/128
Goodness-of-fit on F^2	1.045	1.051
R_1, wR_2 [obs I>2σ (I)]	0.0456, 0.0994	0.0424, 0.0981
R_1, wR_2 (all data)	0.0649, 0.1092	0.0575, 0.1070
residual peak/hole, e. $Å^{-3}$	0.202/-0.282	0.179/-0.173
transmission ratio	0.9707/0.9586	0.9835/0.9786

1. J. Mcmurry, *Acc. Chem. Res.* 1983, **16**, 405-411