Electronic Supplementary Information (ESI)

Molecular Anchors in the Solid State: Restriction of Intramolecular Rotation Boosts Emission Efficiency of Luminogen Aggregates to Unity

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Materials and Instrumentations

Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl under nitrogen immediately prior to use. All the chemicals and other regents were purchased from Aldrich and used as received without further purification. Compound **1**, named 1-(4-bromophenyl)-1,2,2-triphenylethene, was prepared according to previous publication.[1] ^{1}H and ^{13}C NMR spectra were measured on a Bruker AV 300 spectrometer in deuterated dichloromethane using tetramethylsilane (TMS; $\delta = 0$) as internal reference. UV spectra were measured on a Milton Roy Spectronic 3000 Array spectrophotometer. Photoluminescence was recorded on a Perkin-Elmer LS 55 spectrofluorometer. The MALDI-TOF mass spectrum was recorded on a GCT premier CAB048 mass spectrometer. Elemental analysis was performed on an Elementary Vario EL analyzer. Single crystal X-ray diffraction intensity data were collected at 100 K on a Bruker–Nonices Smart Apex CCD diffractometer with graphite monochromated Mo Kα radiation. Processing of the intensity data was carried out using the SAINT and SADABS routines, and the structure and refinement were conducted using the SHELTL suite of X-ray programs (version 6.10). The ground-state geometries were optimized using the density functional (DFT) with B3LYP hybrid functional at the basis set level of 6-31G(d). All the calculations were performed using Gaussian 03 package.

Preparation of Nanoaggregates. Stock THF solutions of the compounds with a concentration of 10^{-4} M were prepared. Aliquots of the stock solution were transferred to 10 mL volumetric flasks. After appropriate amounts of THF were added, water was added dropwise under vigorous stirring to furnish 10^{-5} M solutions with different water contents (0–90 vol %). The PL measurements of the resultant solutions were then performed immediately.

Synthesis

Synthesis of 4-(1,2,2-triphenylvinyl)phenylboronic acid (2): Into a dry THF solution (80 mL) of **1** (4.11 g, 10 mmol) in a 250 mL two-necked round bottom flask was slowly added 7.5 mL (12 mmol) of *n*-butyllithium (1.6 M in hexane) at –78 °C under nitrogen. After stirring at –78 °C for 3 h, 2.4 mL of trimethylborate (20 mmol) was added to the reaction mixture. The mixture was warmed to room temperature and terminated by adding 10 mL of 2 M hydrochloric acid after 12 h. The mixture was poured into water and extracted with dichloromethane. The organic layer was washed with water and dried over magnesium sulfate. After filtration and solvent evaporation, the residue was purified by silica-gel column chromatography using *n*-hexane/ethyl acetate as eluent. White solid of **2** was obtained in 70% yield (2.6 g). ^{1}H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 7.88 (d, 2H, J = 8.1 Hz), 7.13–7.00 (m, 17H), 4.49 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$), δ (TMS, ppm): 148.9, 144.2, 144.1, 144.09, 142.4, 141.4, 135.6, 133.5, 132.0, 131.6, 128.4, 128.3, 127.4, 127.2. MS (MALDI-TOF): m/z 376.2030 (M^+, calcd 376.1635).

General procedures for the synthesis of TPEIq, TPENp, TPEPa TPEAn, and TPEPy. All the compounds were synthesized by a similar procedure shown below in 60–85% yields. A mixture of **2** (1.0 mmol), aryl bromide (ArBr) (1.1 mmol), $Pd(PPh_3)_4$ (0.05 mmol), and potassium carbonate (4.0 mmol) in 100 mL of toluene/ethanol/water (8/1/1 v/v/v) was heated to reflux for 24 h under nitrogen. After filtration and solvent evaporation, the residue was purified by silica-gel column chromatography using hexane/dichloromethane mixture or ethyl acetate as eluent.

Characterization Data: 1-[4-(1,2,2-Triphenylvinyl)phenyl]isoquinoline (TPEIq): Fawn solid; yield 82%. m.p.: 195 °C. ^{1}H NMR (300 MHz, CD_2Cl_2), δ(TMS, ppm): 8.53 (d, 1H, J = 5.7 Hz), 8.01 (d, 1H, J = 9.6 Hz), 7.87 (d, 1H, J = 7.8 Hz), 7.70–7.65 (m, 1H), 7.61 (d, 1H, J = 5.7 Hz), 7.55–7.49 (m, 1H), 7.43 (d, 2H, J = 9.0 Hz), 7.20–7.06 (m, 17H). ^{13}C NMR (75 MHz, CD_2Cl_2), δ(TMS, ppm): 160.9, 144.9, 144.5, 144.4, 142.9, 142.3, 141.4, 138.4, 137.6, 132.1, 132.0, 131.9, 131.8, 130.7, 130.1, 128.5, 128.4, 128.1, 127.8, 127.7, 127.4, 127.3, 120.5. MS (MALDI-TOF): *m*/*z* 460.1752 (M^+, calcd 459.1987). Anal. Calcd for $C_{35}H_{25}N$: C, 91.47; H, 5.48; N, 3.05. Found: C, 91.24; H, 5.56; N, 3.06.

1-[4-(1,2,2-Triphenylvinyl)phenyl]naphthalene (TPENp): White solid; yield 85%. m.p.: 190 °C. ^{1}H NMR (300 MHz, CD_2Cl_2), δ(TMS, ppm): 7.89–7.79 (m, 3H), 7.51–7.36 (m, 4H), 7.24–7.08 (m, 19H). ^{13}C NMR (75 MHz, CD_2Cl_2), δ(TMS, ppm): 144.4, 144.3, 143.3, 141.9, 141.3, 140.5, 139.3, 134.4, 132.1, 131.9, 131.8, 131.6, 129.9, 128.8, 128.3, 128.1, 127.3, 127.0, 126.5, 126.4, 126.3, 125.9. MS (MALDI-TOF): *m*/*z* 458.2551 (M^+, calcd 458.2035). Anal. Calcd for $C_{36}H_{26}$: C, 94.29; H, 5.71. Found: C, 94.09; H, 5.82.

9-[4-(1,2,2-Triphenylvinyl)phenyl]phenanthrene (TPEPa): White solid; yield 80%. m.p.: 200 °C. ^{1}H NMR (300 MHz, CD_2Cl_2), δ(TMS, ppm): 8.76 (d, 1H, J = 7.8 Hz), 8.71 (d, 1H, J = 8.4 Hz), 7.90–7.83 (m, 2H), 7.69–7.51 (m, 5H), 7.29 (d, 2H, J = 7.8 Hz), 7.20–7.08 (m, 17H). ^{13}C NMR (75 MHz, CD_2Cl_2), δ(TMS, ppm): 144.5, 144.4, 143.7, 142.1, 141.5, 139.5, 139.2, 132.3, 132.1, 132.0, 131.9, 131.7, 131.3, 130.6, 130.1, 129.3, 128.5, 128.4, 128.0, 127.6, 127.5, 127.3, 127.2, 123.6, 123.2. MS (MALDI-TOF): *m*/*z* 508.2397 (M^+, calcd 508.2191). Anal. Calcd for $C_{40}H_{28}$: C, 94.45; H, 5.55. Found: C, 94.06; H, 5.57.

9-[4-(1,2,2-Triphenylvinyl)phenyl]anthracene (TPEAn): White solid; yield 69%. m.p.: 301 °C. ^{1}H NMR (300 MHz, CD_2Cl_2), δ(TMS, ppm): 8.45 (s, 1H), 8.03 (d, 2H, J = 8.4 Hz), 7.59 (d, 2H, J = 8.7 Hz), 7.48–7.43 (m, 2H), 7.38–7.33 (m, 2H), 7.25–7.13 (m, 19H). ^{13}C NMR (75 MHz, CD_2Cl_2), δ(TMS, ppm): 144.6, 144.4, 144.2, 143.9, 142.3, 137.6, 137.5, 132.2, 132.1, 132.03, 132.00, 131.9, 131.2, 130.8, 129.0, 128.51, 128.45, 128.4, 127.4, 127.3, 127.1, 126.0, 125.9. MS (MALDI-TOF): *m*/*z* 508.2436 (M^+, calcd 508.2191). Anal. Calcd for $C_{40}H_{28}$: C, 94.45; H, 5.55. Found: C, 94.14; H, 5.57.

1-[4-(1,2,2-Triphenylvinyl)phenyl]pyrene (TPEPy): White solid; yield 63%. m.p.: 303 °C. ^{1}H NMR (300 MHz, CD_2Cl_2), δ (TMS, ppm): 8.21–8.16 (m, 3H), 8.11–7.93 (m, 6H), 7.37 (d, 2H, *J* = 8.7 Hz), 7.22–7.08 (m, 17). ^{13}C NMR (75 MHz, CD_2Cl_2), δ (TMS, ppm): 144.5, 144.4, 144.3, 143.4, 142.1, 141.4, 139.8, 138.3, 132.2, 131.7, 131.2, 130.6, 129.1, 128.4, 128.2, 128.1, 128.0, 127.2, 126.7, 126.0, 125.7, 125.6, 125.4, 125.3. MS (MALDI-TOF): *m*/*z* 532.2513 (M^+, calcd 532.2191). Anal. Calcd for $C_{42}H_{28}$: C, 94.70; H, 5.30. Found: C, 94.64; H, 5.29.

Synthesis of 9-[4-(1,2,2-Triphenylvinyl)phenyl]carbazole (TPECa): *n*-Butyllithium (1.6 M in hexane, 3.8 mL, 6 mmol) was added dropwise into a THF solution (50 mL) of **1** (2 g, 5 mmol) at –78 °C. After stirring at –78 °C for 3 h, iodine (1.4 g, 5.5 mmol) was added into the solution in three portions. After warmed to room temperature and stirred for 2 h, the mixture was poured into water and extracted with dichloromethane. The organic layer was washed by saturated sodium thiosulfate solution and water, and dried over magnesium sulfate. After filtration and solvent evaporation, the crude product **3** was purified by flash silica-gel column chromatography using hexane as eluent. Compound **2** was then added into a solution of carbazole (1 g, 6 mmol), copper (0.32 g, 5 mmol), potassium carbonate (1 g, 7.5 mmol), and 18-crown-6 (0.027g, 0.1 mmol) in 80 mL DMF, and the mixture was stirred at 170 °C for 24 h under nitrogen. The reaction mixture was cooled to room temperature and filtered. The filtrate was poured into water and extracted with dichloromethane. The organic layer was washed with water and dried over magnesium sulfate. After filtration and solvent evaporation, the residue was purified by silica-gel column chromatography using hexane/dichloromethane as eluent. White solid; yield 32%. m.p.: 205 °C. ^{1}H NMR (300 MHz, CD_2Cl_2), δ (TMS, ppm): 8.13–8.07 (m, 4H), 7.45–7.41 (m, 6H), 7.40–7.10 (m, 17H). ^{13}C NMR (75 MHz, CD_2Cl_2), δ (TMS, ppm): 144.2, 144.1, 144.0, 143.6, 142.5, 141.4, 140.8, 140.1, 136.4, 133.4, 132.1, 128.4, 127.4, 126.8, 126.5, 124.0, 121.0, 120.9, 120.5, 120.1, 111.3, 110.5. MS (MALDI-TOF): *m*/*z* 497.3266 (M^+, calcd 497.2143). Anal. Calcd for $C_{38}H_{27}N$: C, 91.72; H, 5.47; N, 2.81. Found: C, 91.55; H, 5.60; N, 2.64.

Deposited Crystal Data Numbers: CCDC 753334–753339 for TPEPy, TPEAn, TPEPa, TPENp, TPECa, and TPEIq, respectively.

Table S1. Summary of crystal data and intensity collection parameters for TPEIq, TPECa, and TPENp.

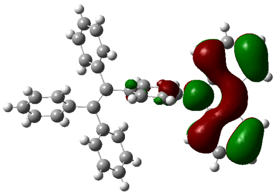
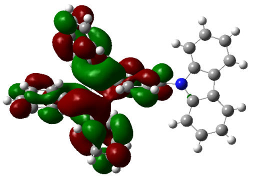
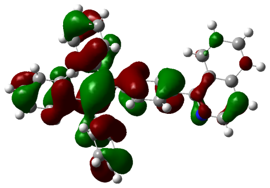
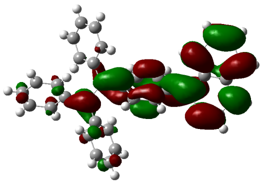
	TPEIq	TPECa	TPENp
Empirical formula	$C_{35}H_{25}N$	$C_{38}H_{27}N$	$C_{36}H_{26}$
Mol wt	459.56	497.61	458.57
Crystal dimensions, mm	0.40 × 0.10 × 0.08	0.40 × 0.16 × 0.14	0.25 × 0.12 × 0.10
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	P-1	P-1	P2(1)/n
a, Å	9.3196(5)	9.4375(8)	9.1633(8)
b, Å	9.3671(5)	9.5683(7)	28.882(3)
c, Å	14.8298(8)	15.5001(12)	19.778(2)
α, deg	88.746(4)	83.076(6)	90
β, deg	86.170(4)	81.063(7)	101.303(10)
γ, deg	75.274(4)	85.554(7)	90
V, Å^3	1249.27(12)	1370.13(19)	5133.0(9)
Z	2	2	8
$D_{\text{calcd.}}$, g cm^3	1.222	1.206	1.187
F_{000}	484	1376	1936
Temp, (K)	173(2)	173(2)	173(2)
Radiation (λ), Å	1.54178	1.54178	1.54178
μ (Mo Kα) mm^{-1}	0.534	0.527	0.507
$2\theta_{\text{max}}$, deg (completeness)	66.5 (95.3%)	66.5 (97.3%)	66.5 (88.8%)
No. of collected reflns.	6612	7122	12975
No. of unique reflns.(R_{int})	4286 (0.0283)	4816 (0.0291)	8184 (0.0621)
Data/restraints/parameters	4286/119/389	4816/0/352	8184/120/625
R_1, wR_2 [obs I > 2σ (I)]	0.0453, 0.1161	0.0404, 0.1066	0.0752, 0.1445
R_1, wR_2 (all data)	0.0637, 0.1247	0.0488, 0.1105	0.1884, 0.1753
Residual peak/hole e.Å^{-3}	0.150/–0.132	0.189/–0.185	0.278/–0.204
Transmission ratio	1.00/0.70	1.00/0.85	1.00/0.55
Goodness-of-fit on F^2	1.025	1.035	1.017

Table S2. Summary of crystal data and intensity collection parameters for TPEPa, TPEAn, and TPEPy.

	TPEPa	TPEAn	TPEPy
Empirical formula	$C_{40}H_{28}$	$C_{40}H_{28}$	$C_{42}H_{28}$
Mol wt	508.62	508.62	532.64
Crystal dimensions, mm	0.30 × 0.28 × 0.04	0.40 × 0.18 × 0.04	0.28 × 0.20 × 0.04
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	P2(1)/c	P-1	I2/a
a, Å	17.2911(10)	9.4850(8)	16.7865(17)
b, Å	9.0613(5)	9.6830(9)	9.2933(6)
c, Å	18.1015(10)	15.5796(14)	36.414(5)
α, deg	90	79.592(8)	90
β, deg	94.720(6)	83.901(7)	91.020(12)
γ, deg	90	85.662(7)	90
V, Å^3	2826.5(3)	1397.0(2)	5679.8(10)
Z	4	2	8
$D_{\text{calcd.}}$, g cm^3	1.195	1.209	1.246

F_{000}	1072	536	2240
Temp, (K)	100(2)	173(2)	173(2)
Radation (λ), Å	1.54178	1.54178	1.54178
μ (Mo Kα) mm^{-1}	0.511	0.517	0.534
$2\theta_{\max}$, deg (completeness)	66.5 (90.1%)	66.5 (97.3%)	66.5 (94.4%)
No. of collected reflns.	7739	7906	7833
No. of unique reflns.(R_{int})	4572 (0.1003)	4897 (0.0363)	4814 (0.0657)
Data/restraints/parameters	4572/0/356	4897/0/361	4814/0/379
R_1, wR_2 [obs I > 2σ (I)]	0.0785, 0.0949	0.0378, 0.0823	0.0553, 0.0946
R_1, wR_2 (all data)	0.1703, 0.1090	0.0573, 0.0866	0.1435, 0.1135
Residual peak/hole e.Å^{-3}	0.220/–0.205	0.128/–0.151	0.130/–0.168
Transmission ratio	1.00/0.79	1.00/0.87	1.00/0.64
Goodness-of-fit on F^2	1.012	1.015	1.008

Table S3. B3LYP/6-31G(d) calculated molecular orbital amplitude plots of HOMO and LUMO energy levels of TPEIq and TPECa.

	HOMO	LUMO
TPECa		
TPEIq		

Reference

1 (*a*) M. Banerjee, S. J. Emond, S. V. Lindeman and R. Rathore, *J. Org. Chem.,* 2007, **72**, 8054; (*b*) Z. Zhao, S. Chen, J. W. Y. Lam, P. Lu, Y. Zhong, K. S. Wong, H. S. Kwok and B. Z. Tang, *Chem. Commun.*, 2010, **46**, 2221