Enlarged Tetrasubstituted Alkenes With Enhanced Thermal and Optoelectronic Properties

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Table S1 EL performances of devices based on 2ADFE and 2TDFE.

Experimental Section

Materials and Instrumentations

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.

¹H and ¹³C NMR spectra were measured on a Bruker AV 400 spectrometer in CDCl₃ or CD₂Cl₂ using tetramethylsilane (TMS; $\delta = 0$) as internal reference. Photoluminescence spectra were recorded on a Perkin-Elmer LS 55 spectrofluorometer. The fluorescence lifetime measurement was performed on the Edinburgh FLS920 spectrofluorimeter with a hydrogen flash lamp as the excitation source on the same spectrofluorometer. High resolution mass spectrum (HRMS) was recorded on a GCT premier CAB048 mass spectrometer operating in MALDI-TOF mode. Thermogravimetric analysis (TGA) was carried on a TA TGA Q5500 under dry nitrogen at a heating rate of 20 °C/min. Thermal transitions were investigated by differential scanning calorimetry (DSC) using a TA DSC Q1000 under dry nitrogen at a heating rate of 10 °C/min.

Cyclic voltammogram was recorded on a Princeton Applied Research (model 273A) at room temperature. The working and reference electrodes were glassy carbon and Ag/AgNO₃ (0.1 M in acetonitrile), respectively. All the solutions were deactivated by bubbling nitrogen gas for a few minutes prior to electrochemical measurements. The oxidation potential of ferrocene was measured to be 0.05 eV, and the onset oxidation potential of 2ADFE was found at 0.52 eV (Figure S14). The formula used to estimate the HOMO level is as follows:

HOMO = $-e(E_{onset-ox} + 4.8 - E_{ferrocene})$

For 2ADFEE, the HOMO = -e (0.52 + 4.8 - 0.05)V \approx -5.3 eV.

For 2TDFE, as shown in Figure S16 the CV spectrum, the HOMO level derived from the onset oxidation potential is of -5.5 eV.

The absolute fluorescence quantum yields were measured by an integrating sphere mounted in an Edinburgh FPLS 920 fluorescence spectrophotometer. The

fluorescence quantum yield is the percentage of photons emitted by a bulk sample when a given number of photons are absorbed by the sample, *i.e.* the number of photons emitted divided by the number of photons absorbed by a sample. The number of photons absorbed by a bulk sample is equal to the number of photons incident on the sample minus the photons passing through and not being absorbed by it. Thus the quantum yield can be represented simply in the equation below:

$$\eta_{\parallel} = \frac{\varepsilon}{\alpha} = \frac{\int L_{emission}}{\int E_{reflector} - \int E_{sample}}$$

Where η is the quantum yield;

 ε is the number of photons emitted by the sample; α is the number of photons absorbed by the sample;

 L_{emission} is the luminescence emission spectrum of the sample, collected using the sphere;

 $E_{\text{reflector}}$ is the spectrum of the light used for excitation with only the standard reference reflector in the sphere, collected using the sphere;

 E_{sample} is the spectrum of the light used to excite the sample, collected using the sphere.

During a typical measurement procedure, the complete emission spectrum of the sample (Sample Emission, $L_{emission}$), the spectra of the excitation light recorded with the sample in place (Sample Scatter, E_{sample}) and the spectra of the excitation light recorded with the standard reference reflector in place (Reference Scatter, $E_{reflector}$) are measured one by one. After combination of these individual spectra, the software will calculate the fluorescence quantum yield. The instrument is calibrated by using standard Alq₃ (Tris(8-hydroxyquinolinato)aluminium) film before formal measurement.

Device fabrication and characterization

EL devices were fabricated on 80 nm-ITO coated glass with a sheet resistance of $25\Omega/\Box$. Prior to load into the pretreatment chamber, the ITO coated glasses were soaked in ultrasonic detergent for 30 min, followed by spraying with de-ionized water for 10 min, soaking in ultrasonic deionized water for 30 min and ovenbake for 1 h. The cleaned samples were treated by CF₄ plasma with a power of 100 W, gas flow of 50 sccm and pressure of 0.2 Torr for 10 s in the pretreatment chamber. The materials

are purified before device fabrication by train sublimation. Then the samples were transferred to the organic chamber with a base pressure of 7×10^{-7} Torr without breaking vacuum for depositing a 60 nm 4,4-bis(1-naphthylphenylamino)biphenyl (NPB), 20 emitter. 10 а nm a nm 2,2',2"-(1,3,5-benzinetriyl)tris(1-phenyl-1-H-benzimidazole) (TPBi), and a 30 nm tris(8-hydroxyquinoline)aluminum (Alq₃), which serve as hole-transporting, hole-blocking, and electron-transporting layers, respectively. The samples were transferred to the metal chamber for cathode deposition which composed of 1 nm LiF capped with 100 nm Al. The light-emitting area was 4 mm² defined by the overlap of cathode and anode. The current density-voltage characteristics of the devices were measured by the HP4145B semiconductor parameter analyzer. The forward direction photons emitted from the devices were detected by a calibrated UDT PIN-25D silicon photodiode. The luminance and external quantum efficiencies of the devices were inferred from the photocurrent of the photodiode. The electroluminescence (EL) spectra were obtained with the PR650 spectrophotometer. All the measurements were carried out under air at room temperature without device encapsulation.

Synthesis



Scheme 1 Synthetic routes to 2ADFE and 2TDFE.

2-bromo-7-benzoylfluorene was synthesized by AlCl₃ catalyzed Friedel-Crafts acylation of **2-bromo-fluorene**.

1,2-bis(2-fluorenyl-7-bromo)-1,2-diphenylethene (2BrDFE): In a two-necked flask equipped with a magnetic stirrer were added 0.52 g (8 mmol) of zinc powder, 0.698 g (2 mmol) of 1,2-bis(2-fluorenyl-7-bromo)-1,2-diphenylethene and 60 mL of THF. TiCl₄ (0.44 mL, 4 mmol) was slowly added by a syringe at 0 °C under nitrogen. The mixture was then heated to reflux overnight. After cooled to room temperature, the reaction was quenched with 10% K₂CO₃ aqueous solution and extracted with CH₂Cl₂. The organic layer was collected and concentrated. The crude product was purified by silica-gel chromatography to give a colorless solid in 85% yield (1.133 g). ¹H NMR (400 MHz, CD₂Cl₂), δ (TMS, ppm): 7.61–7.41 (m, 8H), 7.31–7.19 (m, 3H), 7.14-7.05 (m, 9H), 3.75-3.68 (m, 4H). HRMS (MALDI-TOF): *m/z* 666.0363 [M⁺, calcd 666.0381].

1,2-Bis[4'-(diphenylamino)phenyl-4-yl-(2-fluoren-7-yl)]-1,2-diphenylethene

(2ADFE): Into a stirred mixture of 0.667 g (1 mmol) of 2BrDFE, 1.012 g (3.5 mmol) of (4-(diphenylamino)phenyl)boronic acid, and 10 mL of 2 M Na₂CO₃ solution in 30 mL THF was added 0.02 g of Pd(PPh₃)₄ under nitrogen. The mixture was heated to 80 °C for 12 h. After cooled to room temperature, the solution was extracted with 80 mL of CH₂Cl₂ twice, washed with water, and dried over Na₂SO₄. After filtration and solvent evaporation under reduced pressure, the product was purified by silica-gel column chromatography using hexane/dichloromethane as eluent. A pale yellow solid was obtained in 87% yield (0.866 g). ¹H NMR (400 MHz, CD₂Cl₂), δ (TMS, ppm): 7.73–7.66 (m, 4H), 7.57–7.48 (m, 8H), 7.29–7.22 (m, 10H), 7.12–6.99 (m, 28H), 3.75 (d, 4H); ¹³C NMR (100 MHz, CD₂Cl₂), δ (TMS, ppm): 148.28, 147.69, 144.98, 144.75, 143.70, 143.66, 143.22, 141.87, 140.83, 140.25, 139.57, 139.53, 135.83, 131.95, 130.87, 129.94, 128.21, 126.93, 125.90, 124.95, 124.49, 123.51, 120.56, 119.49, 37.39; MS (MALDI-TOF): m/z 994.3856 [(M)+, calcd 994.4287]. Anal. Calcd. For C44H33N: C, 91.72; H, 5.47; N, 2.81. Found: C, 91.39; H, 5.69; N, 2.86.

1,2-diphenyl-1,2-bis(7-(4-(1,2,2-triphenylvinyl)phenyl)-fluoren-2-yl)ethene

(2TDFE): The compound was prepared from 0.667 g (1 mmol) of 2BrDFE, 1.317 g (3.5 mmol) of (4-(1,2,2-triphenylvinyl)phenyl)boronic acid, and 0.02 g of Pd(PPh₃)₄ using the same procedure described above. Yellow solid; yield 90% (1.052 g). ¹H NMR (400 MHz, CDCl₃), δ (TMS, ppm): 7.71-7.63 (m, 4H), 7.55-7.46 (m, 4H), 7.40-7.35 (m, 4H), 7.22 (d, 2H, J = 8.4 Hz), 7.15-7.01 (m, 46H), 3.73 (d, 4H); ¹³C NMR (100 MHz, CDCl₃), δ (TMS, ppm): 144.161, 144.102, 143.798, 143.748, 142.922, 142.897, 142.627, 142.560, 142.535, 141.187, 141.052, 140.698, 140.648, 140.555, 139.670, 139.645, 139.106, 131.802, 131.726, 131.423, 131.364, 130.521, 130.521, 130.471, 130.378, 128.053, 127.952, 127.699, 126.427, 126.183, 126.115, 125.660, 123.436, 123.335, 119.982, 119.940, 119.156, 119.123, 119.097, 119.030, 119.005, 36.806. HRMS (MALDI-TOF): *m*/*z* 1169.6068 (M⁺, calcd 1169.5042). Anal. Calcd. For C₉₂H₆₄: C, 94.48; H, 5.52. Found: C, 94.19; H, 5.78.



Figure S1. ¹H NMR spectra of 2ADFE in CD₂Cl₂.



Figure S2. ¹³C NMR spectra of 2ADFE in CD₂Cl₂.



Figure S3. ¹H NMR spectra of 2TDFE in CDCl₃.



Figure S4. ¹³C NMR spectra of 2TDFE in CDCl₃.



Figure S5. High resolution mass spectrum of 2ADFE.



Figure S6. High resolution mass spectrum of 2TDFE.



Figure S7. The TEM images and electron diffraction patterns of (A) 2ADFE and (B) 2TDFE formed in THF/water mixtures with 95% water fractions.



Figure S8. Excitation spectra of 2ADFE (left) and 2TDFE (right) in pure THF solution, in aqueous suspensions and in the solid state, respectively.



Figure S9. UV-vis absorption spectra of 2ADFE in THF/water mixtures with different water fractions.



Figure S10. Decay lifetime curves of 2ADFE (left) and 2TDFE (right) in pure THF solution, aqueous suspensions and the solid state.

From the time-resolved fluorescence at 500 nm of the dye molecules in different state, we can see for both AIE compounds, in pure THF the decay lifetimes are very short (the lifetime τ for 2ADFE is only 0.37 ns and for 2TDFE is 0.35 ns, where the values represent the major decay component and similarly hereinafter). Because the dyes in aqueous mixtures with large water fractions form actually small solid particles, the decay lifetimes in 90 % water mixtures and in solid state are quite similar. (for 2ADFE the lifetime τ in 90 % water mixture is 3.7 ns, in solid state is 3.4 ns; for 2TDFE the lifetime τ in 90 % water mixture is 3.3 ns, in solid state is 4.1 ns) The experimental results are consistent with previous studies of the time-resolved photoluminescence on aggregation-induced emissive chromophores (Y. Ren, et.al., *J.*

Phys. Chem. B **2005**, *109*, 1135-1140; M. H. Lee, et.al., *J. Korean Phys. Soc.*, **2004**, 45, 329-332).

The fluorescence quantum yield $\Phi_{\rm F} = \tau/\tau_{\rm r}$, where the PL lifetime τ is related to radiative ($\tau_{\rm r}$) and nonradiative ($\tau_{\rm nr}$) lifetimes by the expression of $1/\tau=1/\tau_{\rm r}+1/\tau_{\rm nr}$. $\tau_{\rm r}$ is the intrinsic property of the molecule. Comparison of the fluorescence decay lifetimes and the fluorescence quantum yields in different state, we can deduce the decay pathways of the excited state of AIE molecule: in well dissolved solutions, it relaxes mainly via a very fast nonradiative intramolecular rotations; while in the aggregate particles and the solid state, the excited molecule decays radiatively with a lifetime of several nanoseconds.



Figure S11. TGA thermograms of (A) 2ADFE and (B) 2TDFE.



Figure. S12 DSC thermograms of 2ADFE (A) and 2TDFE (B) recorded at a heating rate of 10 oC/min. (the second heating and cooling cycle)



Figure S13. Optimized geometry and molecular orbital amplitude plots of HOMO and LUMO energy levels of 2ADFE and 2TDFE.



Figure S14. Cyclic voltammogram of 2ADFE in 0.1 M Bu₄NPF₆/CH₃CN.



Figure S15. Energy level diagrams and device configurations of multilayer EL devices of 2ADFE with and without hole-transporting layers. Abbreviations: NPB = 4,4-bis(1-naphthylphenylamino)biphenyl, TPBi = 2,2',2''-(1,3,5-benzinetriyl)tris(1 -phenyl-1-H-benzimidazole).

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Figure S16. (A) Cyclic voltammogram of 2ADFE in 0.1 M Bu4NPF6/CH3CN; (B) Energy level diagram and device configuration of multilayer EL device of 2TDFE.

Emitter	HTL	V	L	η _c	η _P		CIE
		[V]	[cd/m ²]	[cd/A]	[lm/W]	n _{ext} [%]	[x,y]
2ADFE	\checkmark	3.4 ^b	25550°	13.2 ^c	11.0 ^c	4.3 ^c	
		6.2	100	10.4	5.3	3.4	(0.26, 0.45)
		8.0	1000	8.9	3.5	2.9	
	×	3.4 ^b	19100 ^c	13.7 ^c	11.3 ^c	4.4 ^c	
		6.6	100	10.6	5.3	3.4	(0.26 ,0.44)
		8.2	1000	9.2	3.5	2.9	
2TDFE	\checkmark	3.6 ^b	35160 [°]	15.9 ^c	9.6 ^c	4.9 ^c	(0.25, 0.45)
		5.8	100	14.6	8.0	4.7	
		7.5	1000	14.6	6.3	4.7	

Table S1 EL performances of devices based on 2ADFE and 2TDFE.^a

^a Device configurations, with HTL: ITO/NPB (60 nm)/2ADFE(20 nm)/TPBi (10 nm)/Alq₃ (30 nm)/LiF/Al (200 nm); without HTL: ITO/ 2ADFE(80 nm)/TPBi(10 nm)/Alq₃(30 nm)/LiF/Al(200 nm); Device configuration for 2TDFE: ITO/NPB(60 nm)/2TDFE(20 nm)/TPBi(10 nm)/Alq₃(30 nm)/LiF/Al(200 nm); ^b turn-on voltage; ^c maximum value.