Electronic Supplementary Information

A novel tetraphenylethene-carbazole type compound containing dimesitylboron moiety: aggregation-induced emission enhancement and electroluminescence properties

Heping Shi,*^{a,b} Jinwei Yang,^a Xiuqing Dong,^c Xiaohuan Wu,^a Hongpeng Zhou^a Fangqin Cheng,*^c and Martin M. F. Choi*^d

^aSchool of Chemistry and Chemical Engineering, Shanxi University, 92 Wu Cheng Road, Taiyuan 030006, Shanxi Province, China. E-mail: <u>hepingshi@sxu.edu.cn</u>; Fax: +86-351-7011688; Tel.: +86-351-7010588

^bState Key Laboratory of Luminescent Materials and Devices, South China University of Technology, Guangzhou 510640, Guangdong Province, China

^cState Environmental Protection Key Laboratory of Efficient Utilization Technology of Coal Waste Resources, Shanxi University, 92 Wucheng Road, Taiyuan 030006, Shanxi Province, China. E-mail: <u>cfangqin@sxu.edu.cn</u>; Fax: +86-351-7018813; Tel.: +86-351-7018813

^dPartner State Key Laboratory of Environmental and Biological Analysis, and Department of Chemistry, Hong Kong Baptist University, 224 Waterloo Road, Kowloon Tong, Hong Kong SAR, China. E-mail: <u>mfchoi@hkbu.edu.hk</u>; Fax: +852-34117348; Tel.: +852-34117839

Materials

All reagents were used as received from commercial sources without further purification unless otherwise stated. Tetrahydrofuran (THF) was purified through distillation from Na in the presence of benzophenone. All reactions and manipulations were performed under a nitrogen atmosphere using standard Schlenk techniques.

Instrumentation

Melting points were determined on an X-5 melting point detector. NMR spectra were measured on a Bruker 600 MHz spectrometer. Cyclic voltammetry was acquired on a CHI-600C electrochemical analyser. The measurements were performed with a conventional three-electrode configuration

consisting of a glassy carbon working electrode, a platinum-disk auxiliary electrode and an Ag/AgCl reference electrode. The scan rate was 10 mV/s. UV-vis absorption spectra were obtained from a Shimadzu UV-2450 absorption spectrophotometer. Fluorescence spectra were taken on a Shimadzu RF-5301PC fluorescence spectrometer. Fluorescence quantum yields were determined using a standard actinometry method. Quinine sulfate was used in the actinometer with a known fluorescence quantum yield of 0.55 in 0.10 M sulfuric acid (excited at 350 nm).¹ All measurements were performed at room temperature. Differential scanning calorimetry (DSC) analysis and thermogravimetry analysis (TGA) were performed on a TA Instruments TGA 2050 thermogravimetric analyzer (New Castle, DE, USA) under nitrogen atmosphere at a heating rate of 10 $^{\circ}$ C /min from room temperature to 600 $^{\circ}$ C.

Device fabrication and testing

The multilayer OLED was fabricated by vacuum-deposition method. Organic layers were fabricated by high-vacuum $(5 \times 10^{-4} \text{ Pa})$ thermal evaporation onto a glass (3 cm \times 4 cm) substrate pre-coated with an indium tin oxide (ITO) layer. Glass substrates with patterned ITO electrodes were washed and cleaned through O₃ plasma treatment. Furthermore, a LiF layer was thermally deposited onto the organic material layer, followed by A1 metal deposition as the top layer in a high-vacuum chamber. N,N'-di-1-naphthyl-N,N'-diphenylbenzidine (NPB) was used as the hole-transporting layer (HTL), tris(8-hydroxyquinolinolato) aluminium (Alq₃) was used as the electron-transporting layer (ETL), 2,2',2"-(1,3,5-benzinetriyl) tris(1-phenyl-1-H-benzimidazole) (TPBi) was used as the hole-blocking layer, DTPCZ was used as the emitting layer and LiF/Al was evaporated as the cathode. All organic layers were sequentially deposited. Thermal deposition rates for organic materials, LiF and Al were 0.5, 0.5 and 1.0 Å/s, respectively. The active area of the device is 12 mm². The electroluminescent spectra were measured on a Hitachi MPF-4 fluorescence spectrometer. The voltage-current density (V-J) characteristics of the OLED were recorded on a Keithley 2400 Source Meter. The characterisation of brightness-current-voltage (B-I-V) was measured with a 3645 DC power supply combined with a 1980A spot photometer and was recorded simultaneously. All measurements were done at room temperature.

Theoretical calculation

The ground-state geometry of **DTPCZ** was optimized at B3LYP level with 6-31G (d,p) basis set by using the polarized continuum model (PCM).²⁻⁶ The frontier molecular orbital characteristics were analysed on the optimized structure at the same level. All calculations were carried out in Supercomputing Center of Computer Network Information Center of Chinese Academy of Sciences with the Gaussian 03 program package.⁷

Synthesis of DTPCZ

1-(4-Bromophenyl)-1,2,2-triphenylethene (1) and 1-(4-iodophenyl)-1,2, 2-triphenylethene (2) were

synthesised according to the earlier procedures.^{8,9}

Synthesis of 1-(4-Bromophenyl)-1, 2, 2-triphenylethene

Under a nitrogen atmosphere, *n*-butyllithium (2.2 M, 4.6 mL, 10 mmol) was added dropwise to a solution of diphenylmethane (2.02 g, 12 mmol) in dry THF (50 mL) at 0°C. The resulting orange-red solution was stirred for 1 h at 0°C and then transferred slowly to a solution of 4-bromobenzophenone (2.6 g, 10 mmol) in THF (20 mL) at 0°C. The mixture was allowed to warm to room temperature and stirred for 6 h. The reaction was quenched by adding an aqueous solution of ammonium chloride into the mixture. The organic layer was extracted with CH₂Cl₂. The combined organic layer was dried over anhydrous MgSO₄, filtered and evaporated under reduced pressure to obtain the crude product. The resulting crude product was dissolved in 80 mL toluene, into which a catalytic amount of *p*-toluenesulfonic acid (2.3 g) was added. After being refluxed for 6 h, the mixture was cooled to room temperature, washed with a saturated brine solution, and dried over anhydrous magnesium sulfate. After filtration and solvent evaporation, the residue was purified by silica gel column chromatography with *n*-hexane as the eluent. 1-(4-Bromophenyl)-1,2, 2-triphenylethene was obtained as a white solid in 62% yield (3.06 g). ¹H NMR (600 MHz, CDCl₃) δ (ppm): 7.21 (d, J=8.2Hz, 2H), 7.09 (m, 10H), 7.01 (m, 6H), and 6.90 (d, J=8.6Hz, 2H).

Synthesis of 1-(4-iodophenyl)-1, 2, 2-triphenylethene

An over-dried round-bottom flask containing (2.055g, 0.005 mmol) **1** and 50 mL dry THF was cooled to -78 °C under a nitrogen atmosphere. Then 3.4 mL (7.5 mmol) *n*-BuLi was added slowly, and the reaction was stirred at -78 °C for 10 min before warming to room temperature. After 20 min, the flask was returned to -78 °C, and a solution of iodine (1.9 g) in THF was added dropwise until the red colour persisted. The mixture was allowed to warm to room temperature and stirred for 6 h. The organic layer was extracted with CH_2Cl_2 . The combined organic layer was dried over anhydrous MgSO₄, filtered and evaporated under reduced pressure to obtain the crude product. The crude product was purified by chromatography to obtain a white solid. ¹H NMR (600 MHz, CDCl₃) δ (ppm): 7.4 (d, J=8.8Hz, 2H), 7.08-7.13 (m, 10H), 6.99-7.02 (m, 6H), and 6.76 (d, J=8.1Hz, 2H).

Synthesis of 3-bromo-9-(4-(1, 2, 2-triphenylvinyl) phenyl) carbazole

A mixture of 3-bromocarbazole (2.85 g, 0.01164 mol), **2** (4.432 g, 0.0097 mol), 18-crown-6 (0.512 g, 0.00194 mol), K₂CO₃ (8.03 g, 0.0582 mol) and CuI (0.922 g, 0.00485 mol) was dissolved in DMF. The reaction mixture was heated to 140 °C for 2 days under a nitrogen atmosphere and then poured into water (600 mL) to obtain the precipitate. The precipitate was filtered and washed three times with water. The crude product was purified by column chromatography on silica gel (CH₂Cl₂/hexane) to afford the pure white solid (1.4g, 19.4% yield). ¹H NMR (600 MHz, CDCl3) δ (ppm): 8.17 (s, J=9.8Hz, 2H), 7.48 (d, J=8.98Hz, 2H), and 7.07-7.24 (m, 19H).

Synthesis of 3-dimesityboron-9-(4-(1,2,2-triphenylvinyl) phenyl) carbazole (DTPCZ)

Under a nitrogen atmosphere, 3 (0.677 g) was dissolved in anhydrous THF (60 mL) and cooled to -78 °C, and then *n*-butyllithium (3.07 mL, 4 mmol) was added slowly to solution. Subsequently, the reaction mixture was left to room temperature for an hour and then cooled to -78 °C again. Dimesitylboron fluoride (1.6 g, 6.0 mmol) in THF (20 mL) was added slowly, and the reaction mixture was warmed to room temperature. Then it was stirred for 24 h before being quenched with water. The THF was removed under a reduced pressure and the residue was extracted with CH₂Cl₂. The combined organic layer was dried over anhydrous MgSO₄, filtered and evaporated under reduced pressure to obtain the crude product. The crude product was purified by silica gel column chromatography (CH₂Cl₂/hexane). Light green solid of **DTPCZ** was obtained in 36% yield (0.37 g). ¹H NMR (600 MHz, CDCl₃) δ (ppm): 8.259 (m, 2H), 7.92 (m, 1H), 7.49-7.65 (m, 3H), 7.16-7.36 (m, 19H), 6.85 (d, J=8.1Hz, 4H), 2.336 (d, J=2.69Hz, 6H), 2.045 (d, J=2.33Hz, 12H). ¹³CNMR (600 MHz, CDCl₃) δ (ppm): 146.420, 144.969, 143.897, 143.036, 142.898, 141.067, 140.929, 138.194, 135.853, 135.613, 134.300, 134.293, 134.242, 134.227, 131.143, 131.063, 131.048, 131.033, 130.851, 130.800, 130.749, 130.713, 130.691, 129.714, 129.677, 129.633, 129.123, 129.108, 128.955, 126.119, 125.892, 123.384, 122.939, 113.992, 112.949, and 112.096. MS: *m/z* 745.3. Anal. Calcd for C₅₆H₄₈BN: C 90.19%, H 6.49% and N 1.88%. Found: C 90.13%, H 6.45% and N 1.82%.





Figure S1. UV-vis absorption spectra of **DTPCZ** (5.0 μ M) in various solvents: *n*-hexane (Hex), dichloromethane (CH₂Cl₂), tetrahydrofuran (THF), and acetonitrile (CH₃CN), dimethylsulfoxide (DMSO).



Figure S2. Fluorescence spectra of DTPCZ



Figure S3. SEM image of nano-aggregates of **DTPCZ** obtained from THF-water mixture (1:9). The scale bar is 100 nm. The inset displays the TEM image of the nano-aggregrates of **DTPCZ**. The scale bar is 50 nm.



Figure S4. Photoluminescence spectrum of film of DTPCZ.



Figure S5. The optimal structure and HOMO and LUMO distributions of DTPCZ



Figure S6. TGA curve of DTPCZ.



Figure S7. DSC curve of DTPCZ.



Figure S8. Cyclic voltammogram of **DTPCZ** in THF containing 0.10 M Bu₄NClO₄ as the supporting electrolyte. Two scans are performed.

Table ST Thermal, electroenennear and photophysical data of DTT CE								
$\lambda_{abs}{}^{a}(nm)$	PL ^b (nm)	PL ^c (nm)	T_d^{d} (°C)	T_g^{e} (°C)	T _m ^f (℃)	$E_g^{g}(eV)$	$E_{HOMO}{}^{h}(eV)$	E _{LUMO} ⁱ (eV)
312 and 350	475	465	241	123	202	3.23	-4.98	-1.75
2 . 1			· -					

Table S1 Thermal, electrochemical and photophysical data of DTPCZ

^a Absorption measurement is taken in pure THF.

^b PL emission peak is obtained in 95% water volume fraction of THF-H₂O mixture.

^c PL emission peak is obtained from thin film.

^d Decompositon temperature based on a 5% weight loss from the TGA curve.

^eGlass transition temperature determined from the DSC curve.

^fMelting temperature determined from the DSC curve.

^g Band gap estimated from optical absorption band edge in THF solution.

^h Calculated from the onset oxidation potential in THF containing 0.10 M Bu₄NCl₄.

ⁱ Estimated from $E_{LUMO} = E_{HOMO} + E_g$.

Table S2 Coordinates of DTPCZ from DFT calculations

%chk=dtpcz

%mem=700MW

%nproc=4

opt rb3lyp/6-31g(d,p) scrf=(solvent=water) geom=connectivity

Standard orientation:

Center	Atomic	Atomic	Coordinates (Angstroms)			
Number	Number	Туре	Х	Y	Ζ	
	6		5 267624	0 702416	0.254153	
1	0	0	-5.207024	0.702410	0.234133	
2	0	0	-0.410311	0.002213	0.021239	
5	0	0	-7.746076	0.003890	-0.123011	
	0	0	-3.204643	2.140202	0.043470	
5	0	0	-3.912410	1 497669	0.145601	
07	0	0	-0.440702	-1.467008	-0.103402	
/ 0	0	0	-7.931733	1.742921	-1.00/920	
0	0	0	-9.1650/4	2.334471	-1.104//5	
9	6	0	-10.281550	1.802/82	-0.439187	
10	0	0	-10.110413	0.780291	0.430009	
11	6	0	-8.805/93	0.18/068	0.582779	
12	6	0	-5.848215	-2.310408	0.807930	
13	6	0	-5.903487	-3.700144	0.761038	
14	6	0	-6.552075	-4.297088	-0.322600	
15	6	0	-/.155386	-3.492098	-1.292286	
16	6	0	-/.109883	-2.103004	-1.1/84/8	
1/	6	0	-4.439276	3.066514	-0.026468	
18	6	0	-4.412426	4.409496	0.348319	
19	6	0	-5.193691	4.856468	1.416997	
20	6	0	-6.002080	3.949075	2.105699	
21	6	0	-6.03/993	2.608391	1.722358	
22	6	0	-2.955937	0.269236	1.159328	
23	6	0	-1.686995	-0.296185	1.06/869	
24	6	0	-1.330065	-1.031603	-0.068396	
25	6	0	-2.257403	-1.19/9/9	-1.103/41	
26	6	0	-3.533267	-0.652933	-0.989844	
27	1	0	-0.030339	-1.604827	-0.1/3605	
28	6	0	1.1/4958	-0.915567	-0.100015	
29	6	0	2.248098	-1.83634/	-0.248665	
30	6	0	1.651891	-3.14/555	-0.419/86	
31	6	0	0.246589	-2.966477	-0.368616	
32	6	0	2.176382	-4.433689	-0.596215	
33	6	0	1.300390	-5.510626	-0./11810	
34 25	6	0	-0.090300	-5.313728	-0.646/15	
35	6	0	-0.63/813	-4.043333	-0.4/2319	
36	6	0	1.410255	0.456732	0.05/224	
37	6	0	2.730706	0.885749	0.066899	
38	6	0	3.839888	0.001333	-0.053717	
39	6	0	3.562526	-1.3/2402	-0.208372	
40	5	0	5.307734	0.531256	-0.024141	
41	6	0	6.487033	-0.480115	0.319616	
42	6	0	5.587083	2.066093	-0.336765	
43	6	0	5.190897	2.640494	-1.575567	
44	6	0	5.459699	3.987490	-1.848861	
45	6	0	6.087601	4.821765	-0.921793	
46	6	0	6.466326	4.259935	0.300184	
47	6	0	6.238750	2.912409	0.601645	

10	6	٥	6 502241	1 104056	1 552642
48	6	0	0.303341	-1.184230	1.333043
49 50	6	0	7.550755 8.602176	-2.030960	0.062228
51	6	0	8.002170	-2.295555	0.903236
52	6	0	7 550810	-1.011055	-0.233804
52	6	0	7.559819	-0./12/01	1 0/3035
55 54	6	0	5 /1963/	-1.025612	-1.945055
55	6	0	9 708116	-1.025012	1 201171
55 56	6	0	6 672648	-3.270209 2 416414	1.291171
50 57	6	0	6 331827	6 281714	-1 220927
58	6	0	4 486049	1 844178	-2 658984
50 50	1	0	-7.085336	2 111994	-1 577877
57 60	1	0	-9 305906	3 161286	-1.858745
61	1	0	-10.963325	0.409665	1.002325
62	1	0	-8 747898	-0.655274	1.002525
62 63	1	0	-8.747898	1 853867	1.257855
64	1	0	-5.548500 5.444003	-1.855807	1.710100
0 4 65	1	0	6 503757	-4.310707	0.406762
66	1	0	-0.393737	-3.378943	-0.400702
67	1	0	-7.003293	-3.940219	1 032116
68	1	0	-7.300702	-1.404991	-1.932110
00 60	1	0	-3.822380	5 106382	-0.652726
70	1	0	-3.778331	5.000560	-0.192002
70	1	0	-5.107559	1 282755	2 046738
71	1	0	-0.002473	4.263733	2.940736
72	1	0	-0.003449	0.844014	2.203914
73	1	0	-3.217370	0.044014	2.042013
/4 75	1	0	-0.974802	-0.1/0033	1.0//319
75 76	1	0	-1.972823	-1./40339	-1.999107
70 77	1	0	-4.242339	-0.780240	-1./99400
70	1	0	1 602282	-4.388703	-0.038330
70	1	0	0.755380	-0.515045 6 167800	-0.850210 0.731002
79 80	1	0	-0.755589	-0.107609	-0.751992
81	1	0	-1./11191	-3.8999943	-0.41/910
82	1	0	0.591558	1.100011	0.101775
82 82	1	0	2.927323 A 285221	2 074732	0.179940
84	1	0	4.383321	-2.074732	-0.508821
04 85	1	0	6.062246	4.334103	1.030033
85 86	1	0	7 558402	7.5610/8	2 820820
80	1	0	0.385020	-2.301948	0.068860
88	1	0	9.383020	-1.770417	-0.908809
80	1	0	7 500562	1 040360	1 871366
0 <i>9</i> 00	1	0	6 830822	-0.407004	-2 607780
90 01	1	0	4 622350	-0.407004	-2.007789
91 02	1	0	4.022330	-1.703031	2.407040
92	1	0	4.943983	-0.043029	2.363472
93	1	0	10 660388	-1.170843	0.851778
95 95	1 1	0	Q /Q/17Q	-2.997094	0.031//0
96	1	0	9.707120	<u>-</u> 3 371170	2 371672
97	1	0	7 247842	3 182068	2.371073
98	1	0	7 288206	1 516120	1 807706
99	1	0	5 811281	2 168204	2 597394
11		0	2.011401	2.100204	

100	1	0	7.223137	6.652303	-0.705752
101	1	0	5.487245	6.899740	-0.890837
102	1	0	6.458663	6.454594	-2.293747
103	1	0	3.402704	1.824943	-2.496162
104	1	0	4.815114	0.803899	-2.704055
105	1	0	4.661733	2.293762	-3.640740
106	1	0	-11.256946	2.324574	-0.560071

Table S3 Electroluminescent performances of Device A fabricated with DTPCZ

$\lambda_{EL} (nm)$	$V_{on}(V)$	$L_{max} (cd/m^2)$	$\eta_{c, max} (cd/A)$	CIE (x, y)
464	6.0	4624 (at 16.2V)	4.28 (at 10.5V)	(0.18, 0.21)

The abbreviations are λ_{EL} = electroluminescence emission peak, V_{on} = turn-on voltage at 1 cd m⁻², L_{max} = maximum luminance, $\eta_{C,max}$ = maximum current efficiency. CIE = Commission International de L'Eclairage coordinates.

References

- [1] J. N. Dmas, G. A. Crobys, J. Phys. Chem. 1971, 75, 991.
- [2] P. Hohenberg, W. Kohn, Phys. Rev. B 1964, 136, 864.
- [3] W. Kohn, L. J. Sham, *Phys. Rev. A* 1965, 140, 1133.
- [4] J. B. Foresman, M. H. Gordon, J. A. Pople, M. J. Frisch, J. Phys. Chem. 1992, 96, 135.
- [5] M. Cossi, N. Rega, G. Scalmani, V. Barone, J. Chem. Phys. 2001, 114, 5691.
- [6] M. Cossi, G. Scalmani, N. Rega, V. Barone, J. Chem. Phys. 2002, 117, 43.
- M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, J. J. alvador, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. S. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, GAUSSIAN 03 (Revision B.05), Gaussian, Inc., Pittsburgh, PA, 2003.
- [8] Z. J. Zhao, S. M. Chen, J. W. Y. Lam, C. K. W. Jim, C. Y. K. Chan, Z. M. Wang, P. Lu, C. M. Deng, H. S. Kwok, Y. G. Ma and B. Z. Tang, *J. Phys. Chem. C* 2010, 114, 7963.
- [9] M. Banerjee, S. J. Emond, S. V. Lindeman and R. Rathore, J. Org. Chem. 2007, 72, 8054.