Supporting Information

Highly Efficient Afterglow materials by Heavy Atom Effect of Bromine Effect

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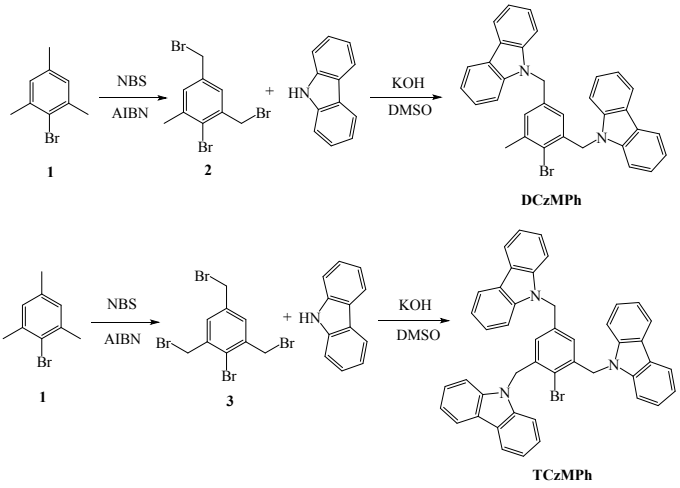
General Considerations

^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra were taken on a Bruker AvanceIII-400. Chemical shifts were reported as delta scale in ppm relative to $CHCl_3$ (δ = 7.26) for ^{1}H NMR and to $CDCl_3$ (δ = 77.0) for ^{13}C NMR. UV-visible absorption spectra were recorded on a TU-1901 double-beam UV-vis spectrophotometer. Fluorescence and phosphorescence spectra in this work were recorded on a Hitachi F-

4600 fluorimeter. Single crystal X-ray diffraction data were collected on a Bruker D8 VENTURE CMOS X-ray diffractometer with a graphite monochromated MoKa radiation (λ= 0.71073 Å). The density functional theory (DFT) calculations were performed using B3LYP/6-31g (d) basis set using Gaussian 09 program. The photographs were taken using a Nikon D3500 camera with a hand-held 365 nm ultraviolet lamp switched on and off. The lifetime and time-resolved emission spectra were obtained on Hitachi F-7000 fluorimeter. Photoluminescence quantum yields were measured by Hamamatsu Absolute PL Quantum Yield Spectrometer C11347.

Synthetic Procedures

Compound **2** and **3** were prepared according to literature methods.[1]



Synthesis of **DCzMPh**

A mixture of carbazole (0.351g, 2.1 mmol), KOH (0.449 g, 8 mmol), and DMSO (20 ml) was stirred for 60 min at room temperature. And **2** (0.357 g, 1.0 mmol) was added slowly. After the completion of the addition, the mixture solution was stirred at room temperature for 10 h. Water (20ml) was then added and the mixture was stirred for 10 min. The mixture was then subjected to suction filtration. The residue was washed several times with and was then dried over vacuum to get crude product. Upon crystallization from dichloromethane/hexanes, colorless crystals were obtained; (yield

90%).

^{1}HNMR (400 MHz, $CDCl_3$), δ [ppm]: 7.32 (d, J = 2.0 Hz, 1H), 7.22 (d, J = 2.0 Hz, 1H), 4.62 (s, 2H), 4.40(s, 1H), 2.43 (s, 4H), 2.48 (s, 3H).

^{13}CNMR (101 MHz, $CDCl_3$) δ: 144.4, 140.2, 139.5, 136.5, 136.5, 127.7, 126.0, 125.7, 123.6, 123.4, 123.1, 122.9, 120.6, 120.3, 119.5, 119.1, 108.8, 108.5, 47.5, 45.9, 23.4.

HR-MS: *m/z* calc. For $[C_{35}H_{25}BrN_2+H]^+$ = 529.1201, found 529.1224.

Synthesis of **TCzMPh**

A mixture of carbazole (0.527g, 3.15 mmol), KOH (0.449 g, 8 mmol), and DMSO (20 ml) was stirred for 60 min at room temperature. And **3** (0.695 g, 1.0 mmol) was added slowly. After the completion of the addition, the mixture solution was stirred at room temperature for 10 h. Water (20ml) was then added and the mixture was stirred for 10 min. The mixture was then subjected to suction filtration. The residue was washed several times with and was then dried over vacuum to get crude product. Upon crystallization from dichloromethane/hexanes, colorless crystals were obtained; (yield 93%).

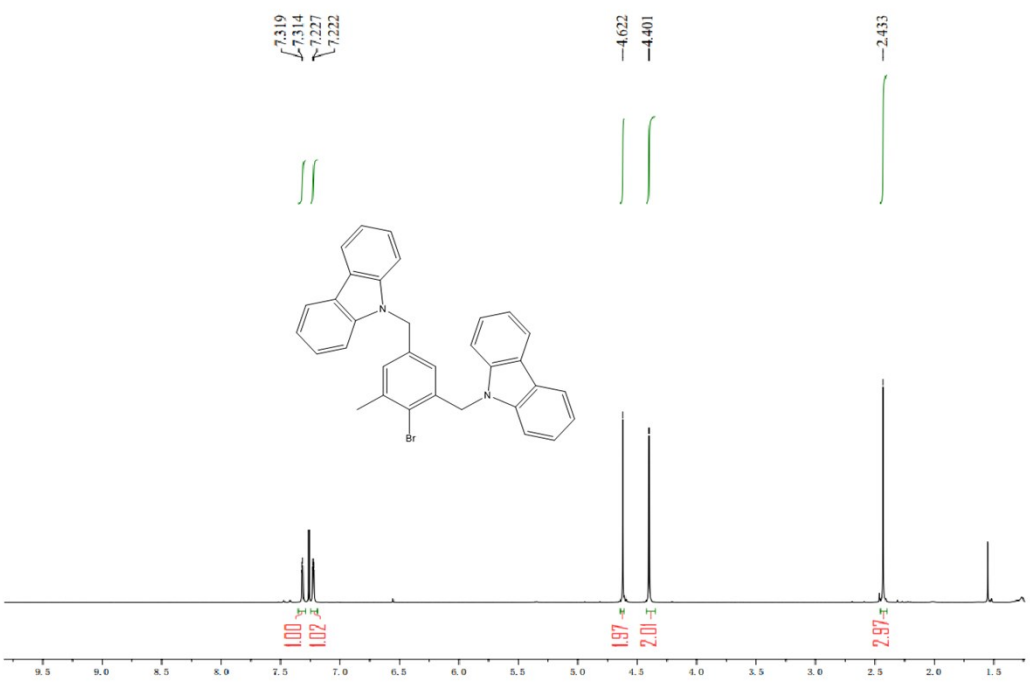
^{1}H NMR (400 MHz, $CDCl_3$), δ [ppm]: 8.08-8.11 (m, 4H),7.82 (d, J = 7.6 Hz, 2H), 7.29-7.33 (m, 4H), 7.22-7.24(m, 4H), 7.123 (d, J = 8.0 Hz, 4H), 7.01-7.05(m, 2H), 6.92-6.96(m, 2H), 6.48 (d, J = 8.0 Hz, 2H), 6.08 (s, 2H), 5.50 (s, 4H), 4.71 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ: 144.4, 140.2, 139.5, 136.5, 136.5, 127.7, 126.0, 125.7, 123.6, 123.4, 123.1, 122.9, 120.6, 120.3, 119.5, 119.1, 108.8, 108.5, 47.5, 45.9, 23.4.

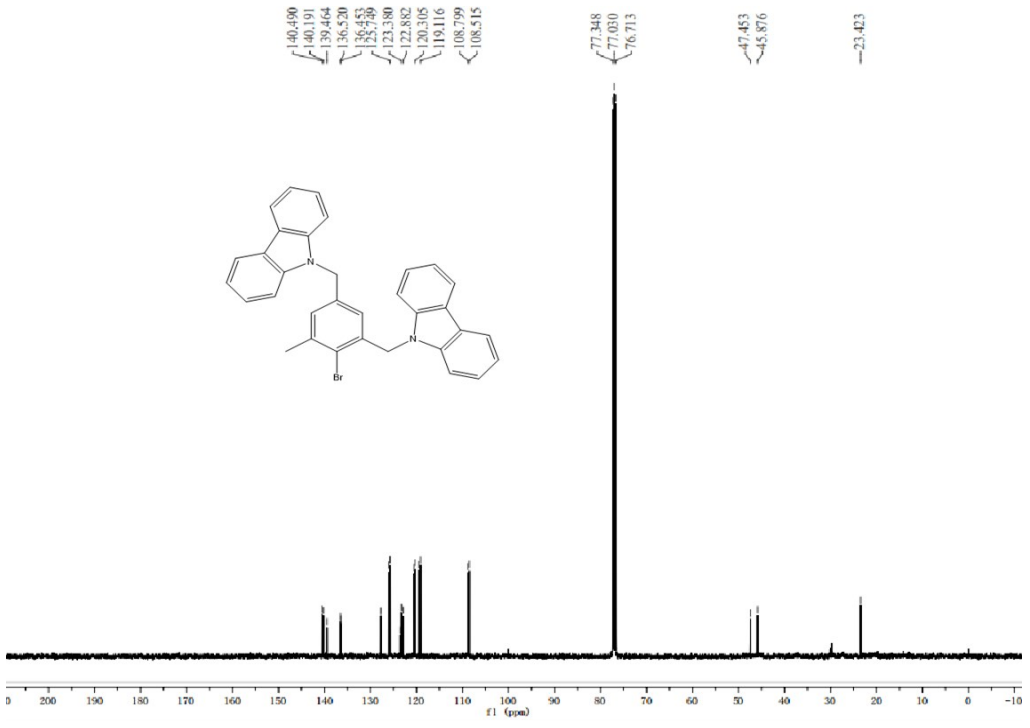
HR-MS: *m/z* calc. For $[C_{45}H_{32}BrN_3+H]^+$ = 694.1780, found 694.1830.

NMR Spectra

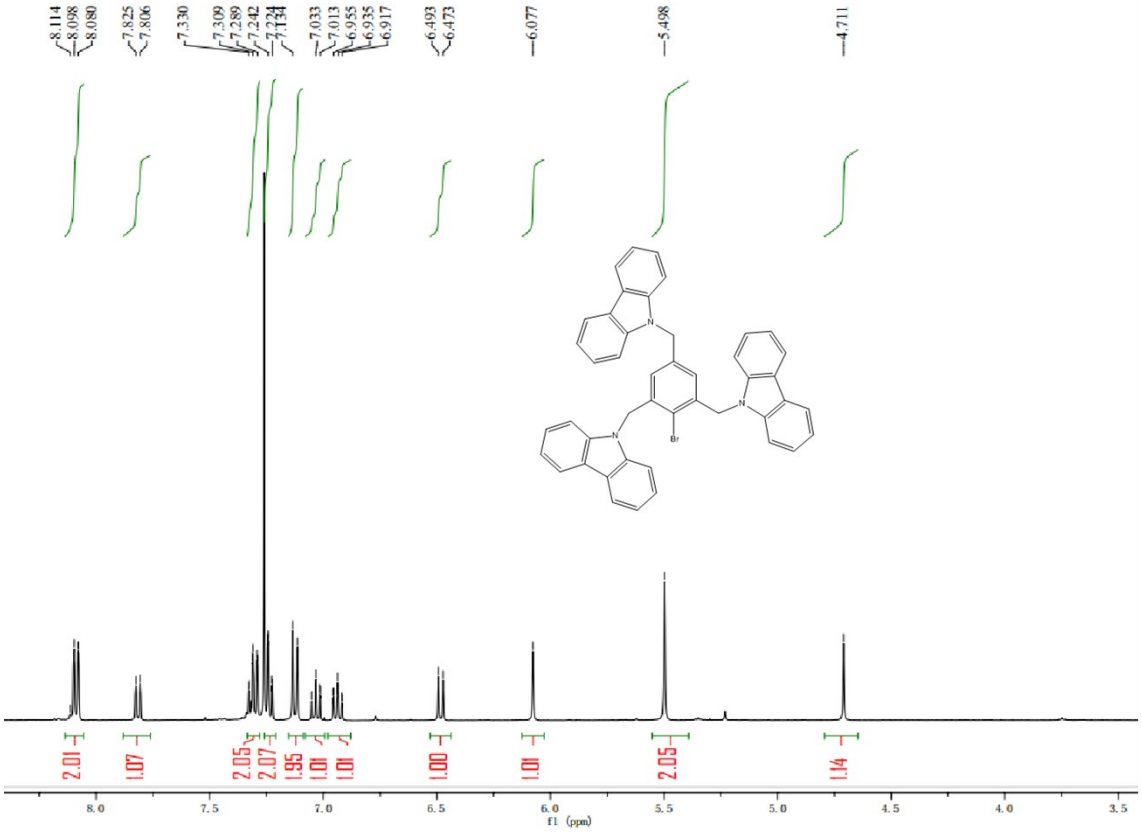
^{1}H NMR spentra of **DCzMPh** (400 MHz, $CDCl_3$)



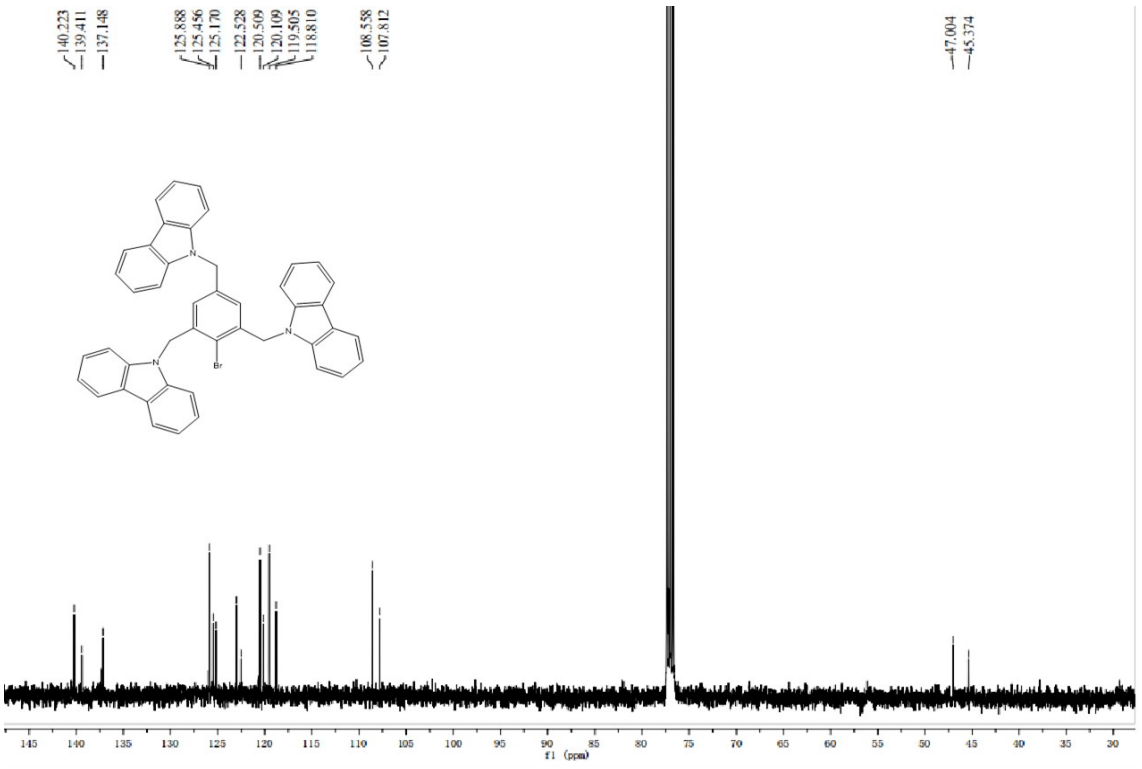
^{13}C NMR spentra of **DCzMPh** (101 MHz, $CDCl_3$)



^{1}H NMR spentra of **TCzMPh** (400 MHz, $CDCl_3$)



^{13}C NMR spentra of **TCzMPh** (101 MHz, $CDCl_3$)



Thermal properties

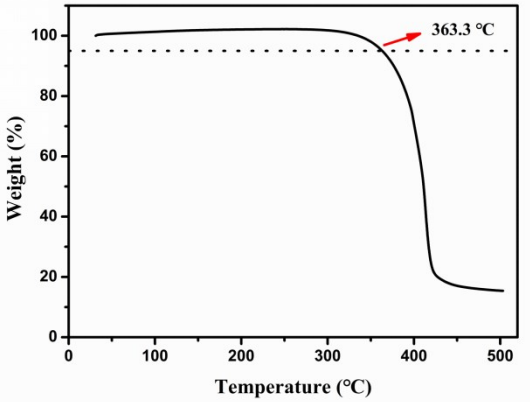


Figure S1. TGA curve of **DCzMPh**

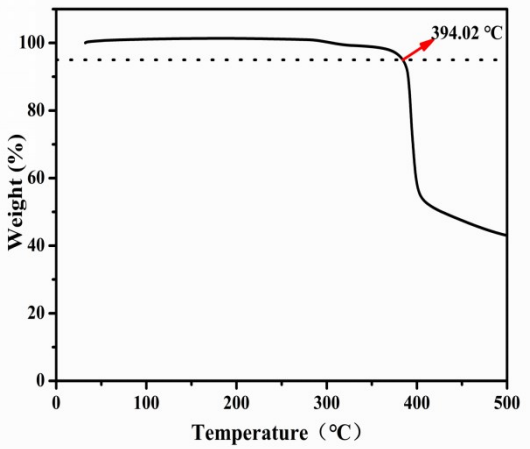
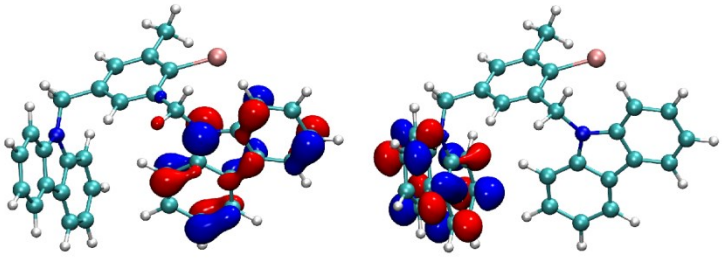
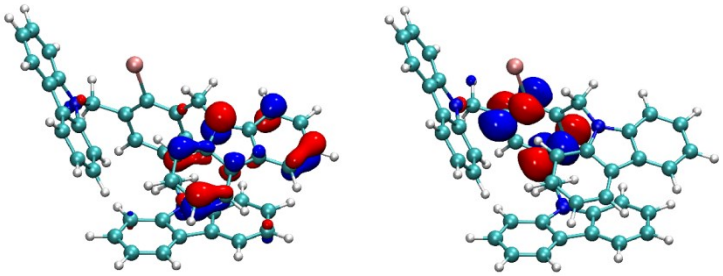


Figure S2. TGA curve of **TCzMPh**

DFT Calculations



HOMO **LUMO**



HOMO LUMO

Figure S3. Calculated spatial distributions of the HOMO and LUMO energy densities of **DCzMPh and TCzMPh** by using density functional theory (DFT) with B3LYP/6-31G* basis set.

Crystallographic Details

CCDC 2022966 (**DCzMPh**) and 2022982 (**TCzMPh**) contain the supplementary crystallographic date for this paper. These data can the obtained free of charge *via* www.ccdc.cam.sa.uk/date_request/cif.

Table S1. Crystal structure refinement data.

Compound	**DCzMPh**	**TCzMPh**
Molecular formula	$C_{33}H_{25}BrN_2$	$C_{45}H_{32}BrN_3$
formula weight	529.12	694.64
Temperature (K)	150(2)	150(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Triclinic	Triclinic
Space group	P-1	P-1
a (Å)	9.1202(6)	8.6776(4)
b (Å)	10.5184(6)	13.1444(5)

c (Å)	13.8101(8)	15.7153(6)
α (˚)	93.211(3)	68.612(2)
β (˚)	95.761(3)	80.333(3)
γ (˚)	108.941(3)	86.144(2)
V (Å^3)	1241.20(13)	1645.33(12)
Z	2	2
ρ_{calc} /Mg·m^{-3}	1.422	1.422
μ / mm^{-1}	1.682	1.288
F(000)	548	716
Reflections collected	7745	10838
Unique reflections	4727	6517
R_{int}	0.0198	0.0405
No. parameters	327	442
GOF	1.069	1.013
R_1 [I > 2σ(I)]	0.0276	0.0464
wR_2 [I > 2σ(I)]	0.0702	0.0944
$\Delta\rho_{max}$ / $\Delta\rho_{min}$ (e Å^{-3})	0.311/-0.459	1.918/-0.437

References

1. Xi Zhao, Wing Yan Ng, Kai-Chung Lau, Alana E. C. Collis and Istvan T. Horvath, *Phys. Chem. Chem. Phys*., **2012**, *14*, 3909 – 3914.