

## Supporting Information

# Thermally Activated Delayed Fluorescence of Carbazole-Benzophenone Dendrimer with Bulky Substituents

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## **1. Experimental section**

**Chemicals.** All chemicals were purchased from Kanto Kagaku Co., Ltd., TCI chemicals or Aldrich and used without further purification unless otherwise noted (solvents for spectroscopic studies were of spectroscopic grade, and solvents for the reactions and device fabrication were of dehydrated grade). I<sub>2</sub>CzTBS was prepared according to the literature method from 3,6-diiido-9H-carbazole.<sup>1</sup> 4,4'-diodobenzophenone was prepared according to the literature method from 4,4'-dibromobenzophenone.<sup>2</sup> All compounds were reprecipitated from MeOH or hexane before the next step.

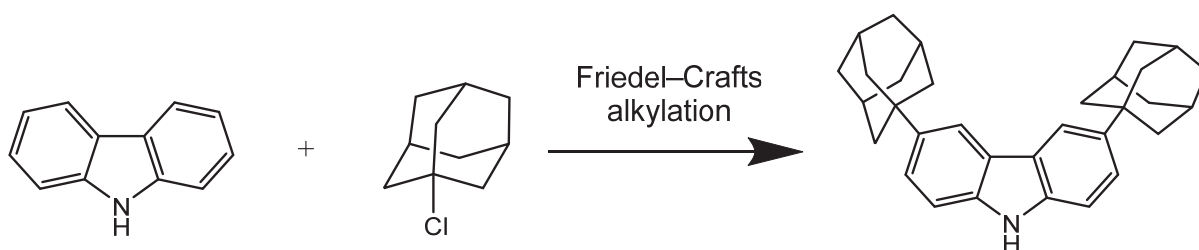
**General.** The NMR spectra were obtained using a JEOL JNM-ECA600 (600 MHz. <sup>1</sup>H NMR and <sup>13</sup>C NMR were measured with TMS as internal standard). The MALDI TOF-MS data were obtained using a JEOL JMS-S3000 in the spiral positive ion mode with Dithranol as the matrix. The UV-vis spectra were recorded using a Shimadzu UV-2600 spectrometer with a quartz cell having a 1cm optical length for the solution at 25 °C. The fluorescence quantum yields were measured by a Hamamatsu Photonics C9920-02 absolute PL quantum yield measurement system (excitation wavelength: 355 nm for film samples). The fluorescence and phosphorescence spectra were measured by a HORIBA JOBIN YVON FluoroMax-plus spectrometer, and the sample temperature was controlled with an Optistat DN(Oxford instruments). The PL lifetime measurements were performed using Horiba FluoroCube (excitation wavelength of 410 nm, pulse width 200 ps). The elemental analysis was performed at the service centre of the elemental analysis of organic compounds, Kyushu University. A preparative scale gel permeation chromatograph, LC-5060 (Japan Analytical Industry Co., Ltd.), was used to isolate each compound with chloroform as the eluent at 14.1 ml/min flow-rate. HOMO levels of the films were measured by photo-electron yield spectroscopy in air using an AC-2 (Riken Keiki). The thermal analysis was performed using a Rigaku Thermoplus TG8110 with flowing nitrogen (100 cc/min), and the temperature rate increase was 10°C/min. AFM images were acquired using a Nanomagnetics ezAFM in the tapping mode and were processed on Gwyddion.

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1) K. Albrecht., K. Matsuoka., K. Fujita, K. Yamamoto, *Angew. Chem. Int. Ed.*, **2015**, *54*, 5677.

2) K. Albrecht, K. Yamamoto, *J. Am. Chem. Soc.* **2009**, *131*, 2244–2251.

## 2. Synthesis



### 3,6-diadamantanyl-9H-carbazole (AdCz)<sup>3</sup>

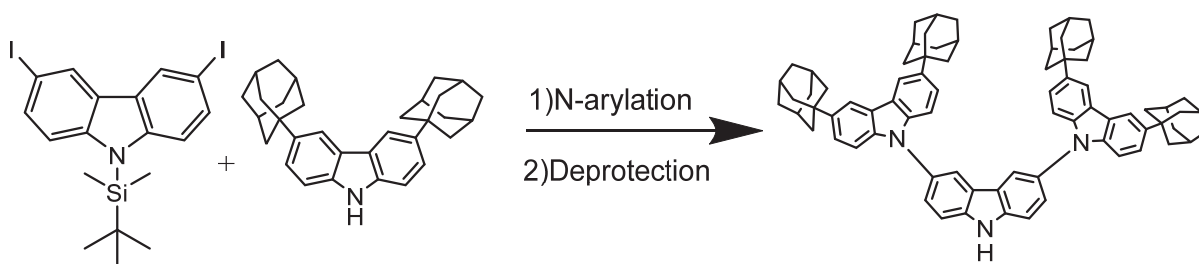
Carbazole (4123 mg, 24.66 mmol) and AlCl<sub>3</sub> (3341 mg, 25.06 mmol) were added to a three neck flask, and then dichloromethane (150 ml) was added under a nitrogen atmosphere. After stirring to dissolve carbazole and AlCl<sub>3</sub>, 1-chloroadamantane (7500 mg, 49.26 mmol) dissolved in dichloromethane (30 ml) was added dropwise. After stirring for 24h at room temperature, the mixture was poured into ice water and extracted with chloroform. The organic layers were combined, dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated. The residue was purified by flash column chromatography using a gradient from 12% to 100% toluene/hexane to give the product. Yield: 28 % (3012 mg)

<sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>) δ 8.06 (d, J = 1.4 Hz, 2H), 7.85 (s, 1H), 7.44 (dd, J = 8.9, 2.1 Hz, 2H), 7.35 (d, J = 8.2 Hz, 2H), 2.15 (s, 6H), 2.06 (d, J = 2.7 Hz, 12H), 1.80-1.84 (m, 12H).

<sup>13</sup>C-NMR (600 MHz, CDCl<sub>3</sub>) δ 142.65, 138.09, 123.49, 122.90, 115.93, 109.98, 43.92, 36.96, 36.14, 29.19.

MALDI TOF-MS(Matrix: Dithranol) Calcd: 435.29 ([M]<sup>+</sup>), Found: 435.36

Anal. Calcd. for C<sub>32</sub>H<sub>37</sub>N: C, 88.22; H, 8.56; N, 3.22. Found: C, 88.12; H, 8.52; N, 3.06.



### 3,3'',6,6''-tetra(adamantan-1-yl)-9'H-9,3':6',9''-tercarbazole (AdG2on) (General procedure for N-arylation reaction, and TBS group cleavage)

AdCz (1000 mg, 2.30 mmol), I<sub>2</sub>CzTBS (583 mg, 1.09 mmol), CuI (31 mg, 0.16 mmol), and K<sub>3</sub>PO<sub>4</sub> (2302 mg, 28.33 mmol) were added to a three-necked flask, and then (±)-trans-1,2-cyclohexanediamine (30 μl, 0.25 mmol) and dioxane (12 ml) were added under a nitrogen atmosphere. After stirring for 18 h at 110 °C, the reaction mixture was cooled to room temperature and diluted with toluene. TBAF (1M THF solution, 1.6 ml) was added, and stirred for 15 min. NH<sub>4</sub>Cl(aq) was added to the mixture and extracted with toluene. The organic layers were combined, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered through silica gel, and concentrated. The product

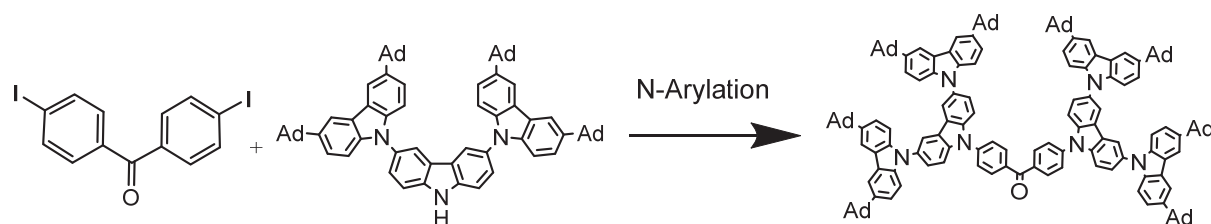
<sup>3</sup> JP Pat., JP 2013-108015, 2013.

was isolated by preparative GPC (eluent: chloroform) and flash chromatography using a gradient from 12% to 100% toluene / hexane. Yield: 20 % (232 mg, 0.22 mmol).

$^1\text{H-NMR}$  (600 MHz,  $\text{THF}_{d8}$ ):  $\delta$  10.87 (s, 1H), 8.31 (d,  $J = 2.1$  Hz, 2H), 8.15 (d,  $J = 2.1$  Hz, 4H), 7.72 (d,  $J = 8.2$  Hz, 2H), 7.57 (dd,  $J = 8.2, 2.1$  Hz, 2H), 7.38 (dd,  $J = 8.9, 2.1$  Hz, 4H), 7.28 (d,  $J = 8.2$  Hz, 4H), 2.07-2.11 (m, 36H), 1.84 (s, 24H)

$^{13}\text{C-NMR}$  (600 MHz,  $\text{THF}_{d8}$ ):  $\delta$  143.35, 141.34, 140.85, 130.76, 126.26, 125.04, 124.25, 123.44, 120.27, 116.55, 112.74, 109.89, 44.80, 37.83, 36.95, 30.39.

MALDI TOF-MS (Matrix: Dithranol) Calcd: 1034.6347 ( $[\text{M}+\text{H}]^+$ ), Found: 1034.6347



### AdG2B

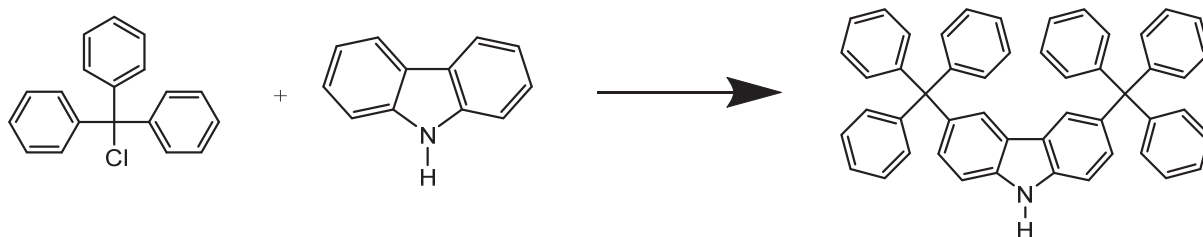
As per the general procedure for the N-arylation reaction, AdG2on (182 mg, 0.18 mmol), 4,4'-diiodobenzophenone (35 mg, 0.08 mmol), CuI (2.50 mg, 0.01 mmol),  $\text{K}_3\text{PO}_4$  (201 mg, 0.95 mmol), ( $\pm$ )-*trans*-1,2-cyclohexanediamine (2.2  $\mu\text{l}$ , 0.02 mmol), and dioxane (1.8 ml) were heated with microwave at 160  $^\circ\text{C}$  for 3h. The reaction mixture was diluted with toluene, and filtered through silica gel. The product was isolated by preparative GPC (eluent: chloroform). Yield: 54 % (100 mg, 0.04 mmol).

$^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.32 (d,  $J = 8.2$  Hz, 4H), 8.27 (d,  $J = 2.3$  Hz, 4H), 8.15 (d,  $J = 1.4$  Hz, 8H), 8.00 (d,  $J = 8.2$  Hz, 4H), 7.80 (d,  $J = 8.7$  Hz, 4H), 7.67 (dd,  $J = 8.7, 1.8$  Hz, 4H), 7.45 (dd,  $J = 8.7, 1.8$  Hz, 8H), 7.37 (d,  $J = 8.7$  Hz, 8H), 2.15 (s, 24H), 2.08 (d,  $J = 2.3$  Hz, 48H), 1.82 (s, 48H)

$^{13}\text{C-NMR}$  (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  194.15, 143.11, 141.42, 140.05, 139.65, 136.23, 132.12, 131.61, 126.59, 126.16, 124.54, 123.34, 123.02, 119.43, 116.04, 111.13, 108.99, 43.89, 36.91, 36.17, 29.16.

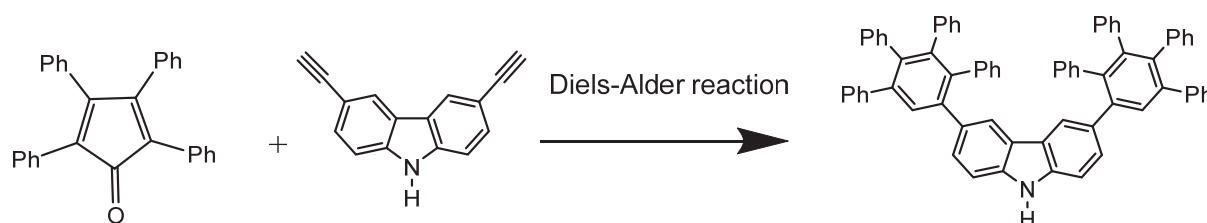
MALDI TOF-MS (Matrix: Dithranol) Calcd: 2247.3072 ( $[\text{M}+\text{H}]^+$ ), Found: 2247.3047





### 3,6-ditrityl-9H-carbazole (TrCz)

Trityl chloride (200036 mg, 71.87 mmol) and 9H-carbazole (5466 mg, 32.69 mmol) were added to a three-neck flask under a nitrogen atmosphere. After heating under reflux for 5 min with stirring to dissolve trityl chloride and 9H-carbazole, followed by heating and stirring at 225 °C for 40 min. The resulting mixture was cooled, diluted with chloroform. After heating under reflux, the precipitate was filtered, washed with chloroform, and recrystallized from chlorobenzene. Yield: 16 % (3508 mg, 5.38 mmol). The NMR spectra were identical to a previous report.<sup>4</sup>



### 3,6-ditetraphenylphenyl-9H-carbazole (TPPhCz)<sup>5</sup>

Tetraphenylcyclopentadienone (2039 mg, 5.30 mmol) and 3,6-Diethynylcarbazole (511 mg, 2.38 mmol) were added to a three-neck flask, and then dry xylene (50 ml) was added under a nitrogen atmosphere. After stirring under reflux for 24h, the reaction mixture was cooled to room temperature. The solvent was evaporated under reduced pressure. The product was isolated by preparative GPC (eluent: chloroform). Yield: 78 % (1723 mg, 1.86 mmol)

<sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>) δ 7.88 (s, 2H), 7.82 (s, 1H), 7.66 (s, 2H), 7.03-7.18 (m, 14H), 6.79-6.92 (m, 30H).

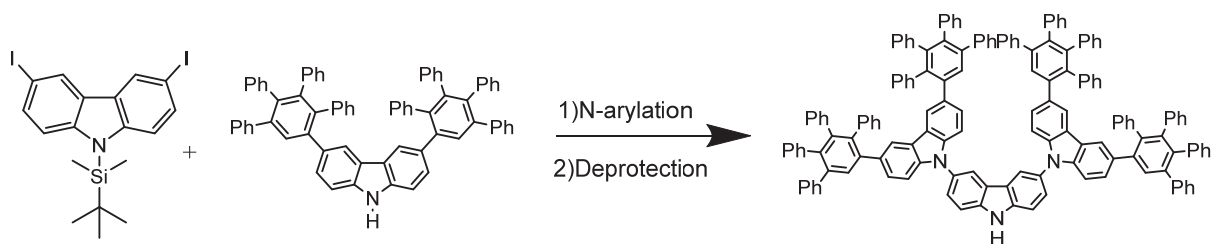
<sup>13</sup>C-NMR (600 MHz, CDCl<sub>3</sub>) δ 141.95, 141.87, 141.43, 140.88, 140.65, 140.42, 140.23, 139.49, 138.96, 138.39, 133.27, 132.15, 131.78, 131.72, 131.65, 130.10, 128.39, 127.71, 127.08, 127.03, 126.73, 126.32, 125.67, 125.59, 125.39, 123.25, 121.60, 109.66.

MALDI TOF-MS(Matrix: Dithranol) Calcd:927.39([M]<sup>+</sup>), Found: 927.43.

Anal. Calcd. for C<sub>72</sub>H<sub>49</sub>N: C, 93.17; H, 5.32; N, 1.51. Found: C, 92.97; H, 5.20; N, 1.61.

4) S. Matsumura, A. R. Hlil, N. Du, C. Lepiller, J. Gaudet, D. Guay, Z. Shi, S. Holdcroft and A. S. Hay, *J. Polym. Sci. A Polym. Chem.*, 2008, **46**, 3860–3868.

5) Q. Xiang, X. Sun, G. Zhu, H. Sun, Y. Wan, Z. Si and Q. Duan, *Eur. J. Inorg. Chem.*, 2012, **2012**, 4012–4019.



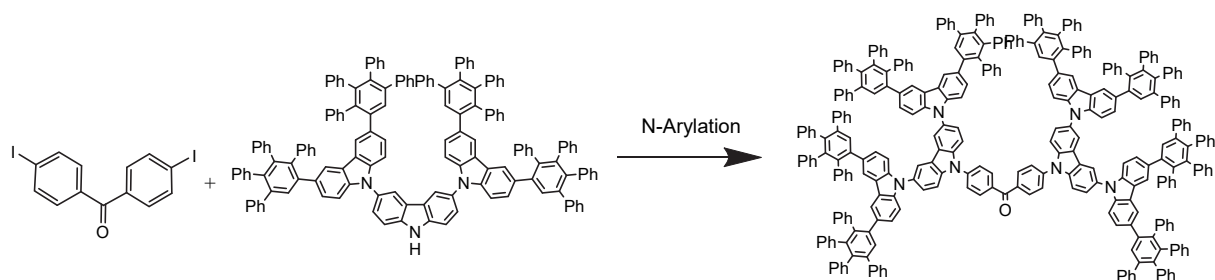
### TPPhG2on

**TPPhCz** (1302 mg, 1.40 mmol), **I<sub>2</sub>CzTBS** (355 mg, 0.67 mmol), CuI (22 mg, 0.12 mmol), and K<sub>3</sub>PO<sub>4</sub> (1437 mg, 6.77 mmol) were added to a three-necked flask, and then (±)-*trans*-1,2-cyclohexanediamine (18 µl, 0.15 mmol) and dioxane (9 ml) were added under a nitrogen atmosphere. After stirring for 18 h at 110 °C, the reaction mixture was cooled to room temperature and diluted with toluene. After filtering through silica gel, the solvent was evaporated under reduced pressure. This residue was placed in a three-necked flask and CuI (21mg, 0.11mmol), and K<sub>3</sub>PO<sub>4</sub> (1478mg, 6.96mmol) were added. Then (±)-*trans*-1,2-cyclohexanediamine (18 µl, 0.15 mmol) and dioxane (9 ml) were added under a nitrogen atmosphere. After stirring for 18 h at 110 °C, the reaction mixture was cooled to room temperature and diluted with toluene. TBAF (1M THF solution, 1 ml) was added, and stirred for 30 min. Additionally, TBAF (1M THF solution, 1 ml) was added, and stirred for 15 min. NH<sub>4</sub>Cl(aq) was added to the mixture and extracted with toluene. The organic layers were combined, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered through silica gel, and concentrated. The product was isolated by preparative GPC (eluent: chloroform). Yield: 43 % (580 mg, 0.29 mmol).

<sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>) δ 8.35 (s, 1H), 8.05 (s, 2H), 7.94 (s, 4H), 7.69 (s, 4H), 7.60 (d, J = 8.9 Hz, 2H), 7.51 (dd, J = 8.6, 1.7 Hz, 2H), 7.13-7.19 (m, 20H), 7.05 (s, 8H), 6.86-6.93 (m, 52H), 6.80 (t, J = 3.8 Hz, 8H)

<sup>13</sup>C-NMR (600 MHz, CDCl<sub>3</sub>) δ 141.96, 141.93, 141.34, 140.90, 140.70, 140.66, 140.39, 140.24, 139.47, 139.11, 138.97, 133.53, 132.24, 131.77, 131.73, 131.66, 130.11, 130.05, 129.87, 128.43, 127.71, 127.15, 127.03, 126.73, 126.34, 126.06, 125.66, 125.38, 123.96, 123.05, 121.65, 119.59, 111.95, 108.82.

MALDI TOF-MS(Matrix: Dithranol) Calcd:2019.8265([M+H]<sup>+</sup>), Found: 2019.8258.



## TPPhG2B

As per the general procedure for the N-arylation reaction, **TPPhG2on** (222 mg, 0.11 mmol), **4,4'-diiodobenzophenone** (23 mg, 0.05 mmol), CuI (2.3 mg, 0.01 mmol), K<sub>3</sub>PO<sub>4</sub> (139 mg, 0.65 mmol), ( $\pm$ )-*trans*-1,2-cyclohexanediamine (1.3  $\mu$ l, 0.01 mmol), and dioxane (0.7 ml) were heated with microwave at 160 °C for 3h. The reaction mixture was diluted with toluene, and filtered through silica gel. The product was isolated by preparative GPC (eluent: chloroform). Yield: 65 % (144 mg, 0.65 mmol).

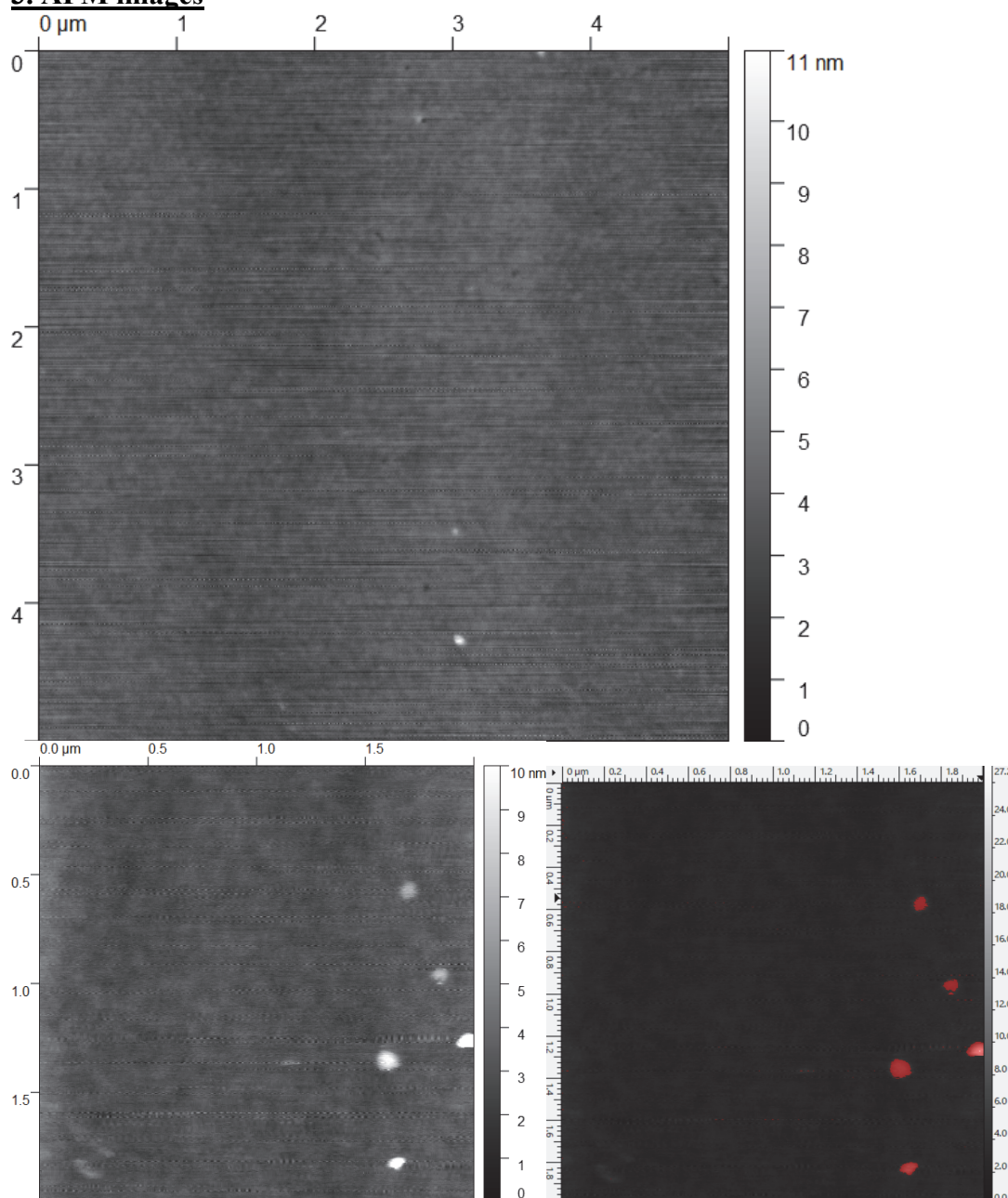
<sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  8.24 (d, J = 8.2 Hz, 4H), 8.16 (d, J = 2.1 Hz, 4H), 7.95 (s, 8H), 7.87 (d, J = 8.2 Hz, 4H), 7.68 (d, J = 6.2 Hz, 12H), 7.56 (dd, J = 8.9, 2.1 Hz, 4H), 7.06-7.19 (m, 56H), 6.79-6.94 (m, 120H)

<sup>13</sup>C-NMR (600 MHz, CDCl<sub>3</sub>)  $\delta$  194.18, 141.95, 141.35, 141.25, 140.94, 140.61, 140.57, 140.39, 140.19, 139.90, 139.47, 139.04, 136.49, 133.73, 132.22, 131.76, 131.70, 131.63, 131.09, 130.09, 128.51, 127.72, 127.16, 127.05, 126.74, 126.36, 125.67, 125.41, 124.45, 123.19, 121.75, 119.73, 111.26, 108.75.

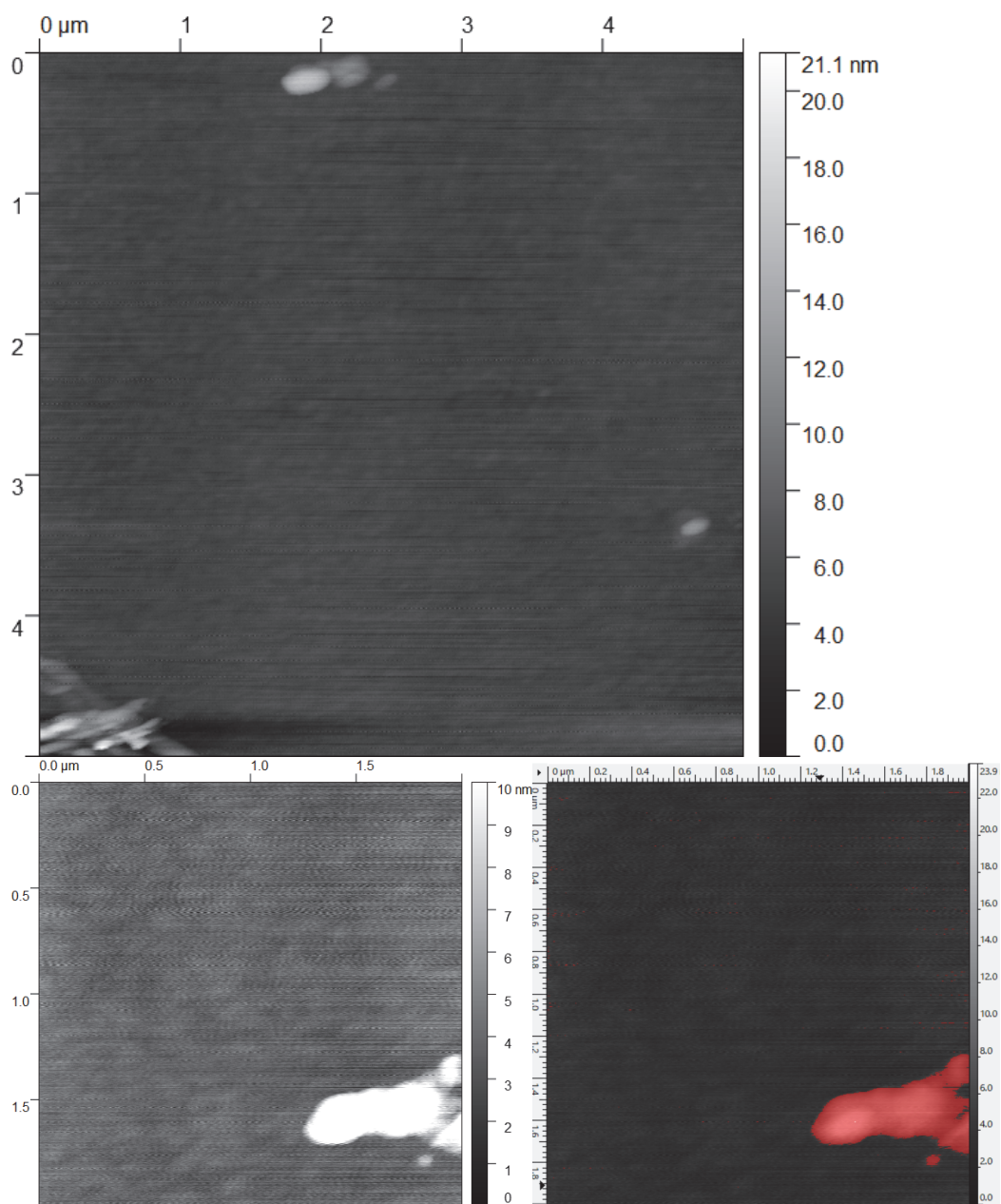
MALDI TOF-MS(Matrix: Dithranol) Calcd:4216.68([M]<sup>+</sup>), Found: 4217.22

Anal. Calcd. for C<sub>325</sub>H<sub>212</sub>N<sub>6</sub>O: C, 92.56; H, 5.07; N, 1.99. Found: C, 92.92; H, 5.07; N, 1.95.

### 3. AFM images



**Figure S1** AFM image of AdG2B film spin-coated on Si substrate from chloroform solution. (top) Wide range scan, and (down left) enlarged image. The roughness (RMS) of the enlarged image was calculated to be 0.5 nm without the debris (red marked parts in the downright image). The images were obtained after 7 days of storage in the ambient conditions.



**Figure S2** AFM image of TPPhG2B film spin-coated on Si substrate from chloroform solution. (top) wide range scan, and (down left) enlarged image. The roughness (RMS) of the enlarged image was calculated to be 0.6 nm without the debris region (red marked parts in the downright image). The images were obtained after 6 days of storage in the ambient conditions.

## 4. TG measurements

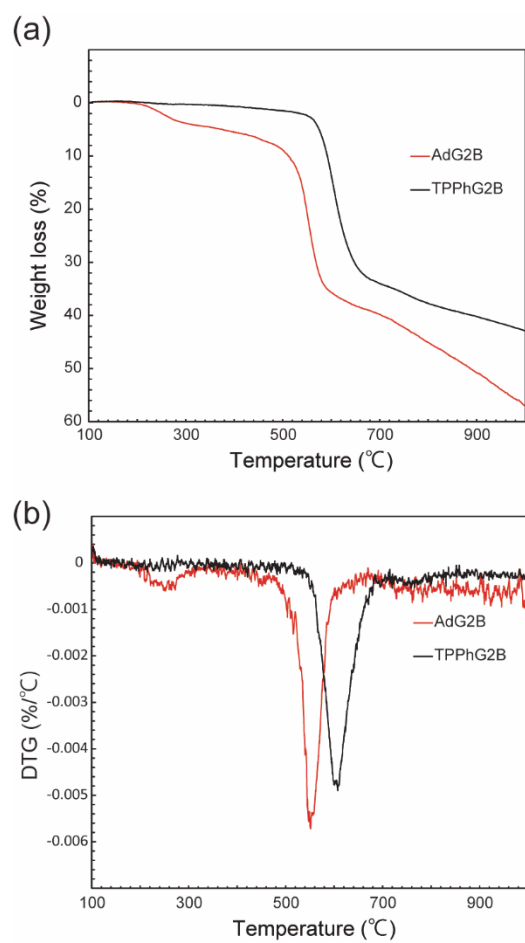


Figure S3 (a)TG, and (b) DTG curves of dendrimers.

## **5. Computation**

### **details**

The equilibrium geometries in the electronic ground and triplet states ( $S_0$  and  $T_1$ ) were determined by the density functional theory (DFT) calculations using the coulomb attenuated B3LYP (CAM-B3LYP) functionals<sup>6</sup> with the 6-31G(d) basis set. The range-separating parameter was changed to  $\mu = 0.20$  following our previous works.<sup>7,8</sup> Geometry optimization in the  $S_1$  state was performed by the time-dependent DFT (TD-DFT) calculations. All calculations were performed within the  $C_2$  symmetry. Solvent effects were taken into account by the polarizable continuum solvation model (PCM) and the parameters were set to represent toluene solvent. During the  $S_1$  geometry optimization, equilibrium solvation is adapted for calculation of the excitation energies. After the geometry optimization, the vertical excitation and emission energies were calculated at the  $S_0$ ,  $S_1$ , and  $T_1$  equilibrium structures (denoted as  $(S_0)_{\min}$ ,  $(S_1)_{\min}$ , and  $(T_1)_{\min}$ ), respectively. All calculations were performed using the Gaussian16 program package<sup>9</sup>.

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<sup>6</sup> Yanai, T.; Tew, D. P.; Handy, N. C. A New Hybrid Exchange–Correlation Functional Using the Coulomb-Attenuating Method (CAM-B3LYP). *Chem. Phys. Lett.* **2004**, *393*, 51–57.

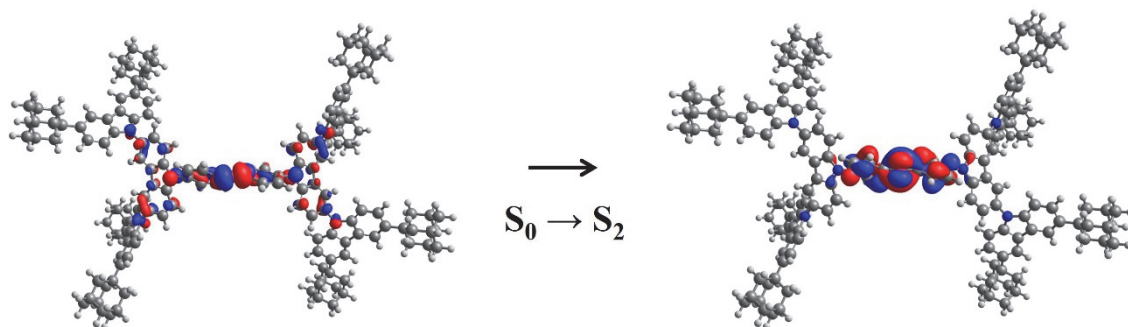
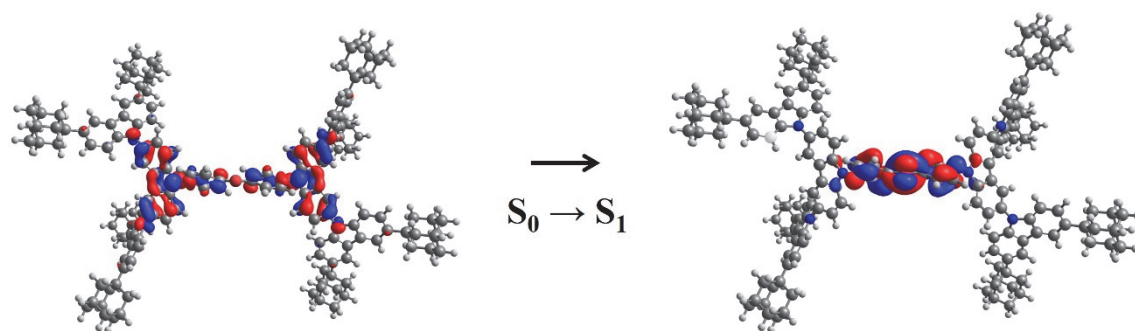
<sup>7</sup> Albrecht, K.; Matsuoka, K.; Yokoyama, D.; Sakai, Y.; Nakayama, A.; Fujita, K.; Yamamoto, K. Thermally Activated Delayed Fluorescence OLEDs with Fully Solution Processed Organic Layers Exhibiting Nearly 10% External Quantum Efficiency. *Chem. Commun.* **2017**, *53*, 2439–2442.

<sup>8</sup> Matsuoka, K.; Albrecht, K.; Nakayama, A.; Yamamoto, K.; Fujita, K. Highly Efficient Thermally Activated Delayed Fluorescence Organic Light-Emitting Diodes with Fully Solution-Processed Organic Multilayered Architecture: Impact of Terminal Substitution on Carbazole–Benzophenone Dendrimer and Interfacial Engineering. *ACS Appl. Mater. Interfaces* **2018**, *10*, 33343–33352.

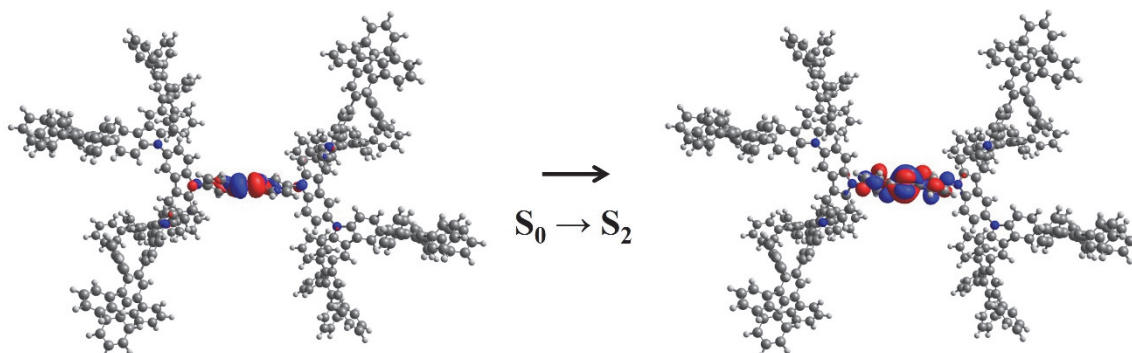
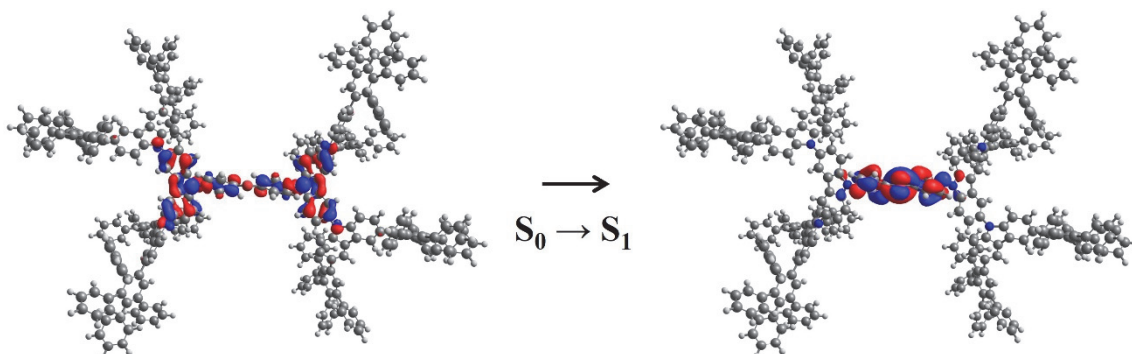
<sup>9</sup> Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, a. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, a. F.; Sonnenberg, J. L.; Williams; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery Jr., J. a.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. a.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, a. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. Gaussian 16, Revision C.01. Gaussian Inc.: Wallin 2016.



### AdG2B



### TPPhG2B



**Figure S4** Dominant natural transition orbital (NTO) pairs for the  $S_1$  and  $S_2$  transitions in toluene at  $(S_0)_{\min}$  for AdG2B and TPPhG2B, where the “hole” is on the left and the “particle” on the right.



**Table S1.** The  $S_0$ ,  $S_1$ ,  $T_1$  Energies at  $(S_0)_{\min}$ ,  $(S_1)_{\min}$ , and  $(T_1)_{\min}$ , and  $\Delta E_{ST} = E(S_1) - E(T_1)$  (in eV) at  $(S_1)_{\min}$  and  $(T_1)_{\min}$  and Vertical Excitation and Emission Wavelengths ( $\lambda_{\text{ex}}$  and  $\lambda_{\text{em}}$  in nm), and Oscillator Strength,  $f_1$  and  $f_2$  for  $S_0 \rightarrow S_1$  and  $S_0 \rightarrow S_2$  transition, respectively at  $(S_0)_{\min}$ .

		$S_0$	$S_1$	$S_2$	$T_1$	$T_2$	$\Delta E_{S-T}$	$\lambda_{\text{ex}}$	$\lambda_{\text{em}}$	$f_1$	$f_2$
<b>AdG2B</b>	$(S_0)_{\min}$	0.00	3.58	3.67	3.18	3.50		347		0.82	0.07
	$(S_1)_{\min}$	0.35	3.30	3.71	3.04	3.53	0.25 <sup>a</sup>		420		
	$(T_1)_{\min}$	0.44	3.41	3.67	2.83	3.48	0.58 <sup>b</sup>				
<b>TPPhG2B</b>	$(S_0)_{\min}$	0.00	3.62	3.69	3.19	3.71		342		0.92	0.03
	$(S_1)_{\min}$	0.19	3.41	3.53	3.09	3.43	0.32 <sup>a</sup>		385		
	$(T_1)_{\min}$	0.44	3.41	3.71	2.83	3.48	0.58 <sup>b</sup>				

<sup>a</sup>  $\Delta E_{ST} = E(S_1) \text{ (at } (S_1)_{\min}) - E(T_1) \text{ (at } (S_1)_{\min})$

<sup>b</sup>  $\Delta E_{ST} = E(S_1) \text{ (at } (S_1)_{\min}) - E(T_1) \text{ (at } (T_1)_{\min})$

## 6. PL spectra

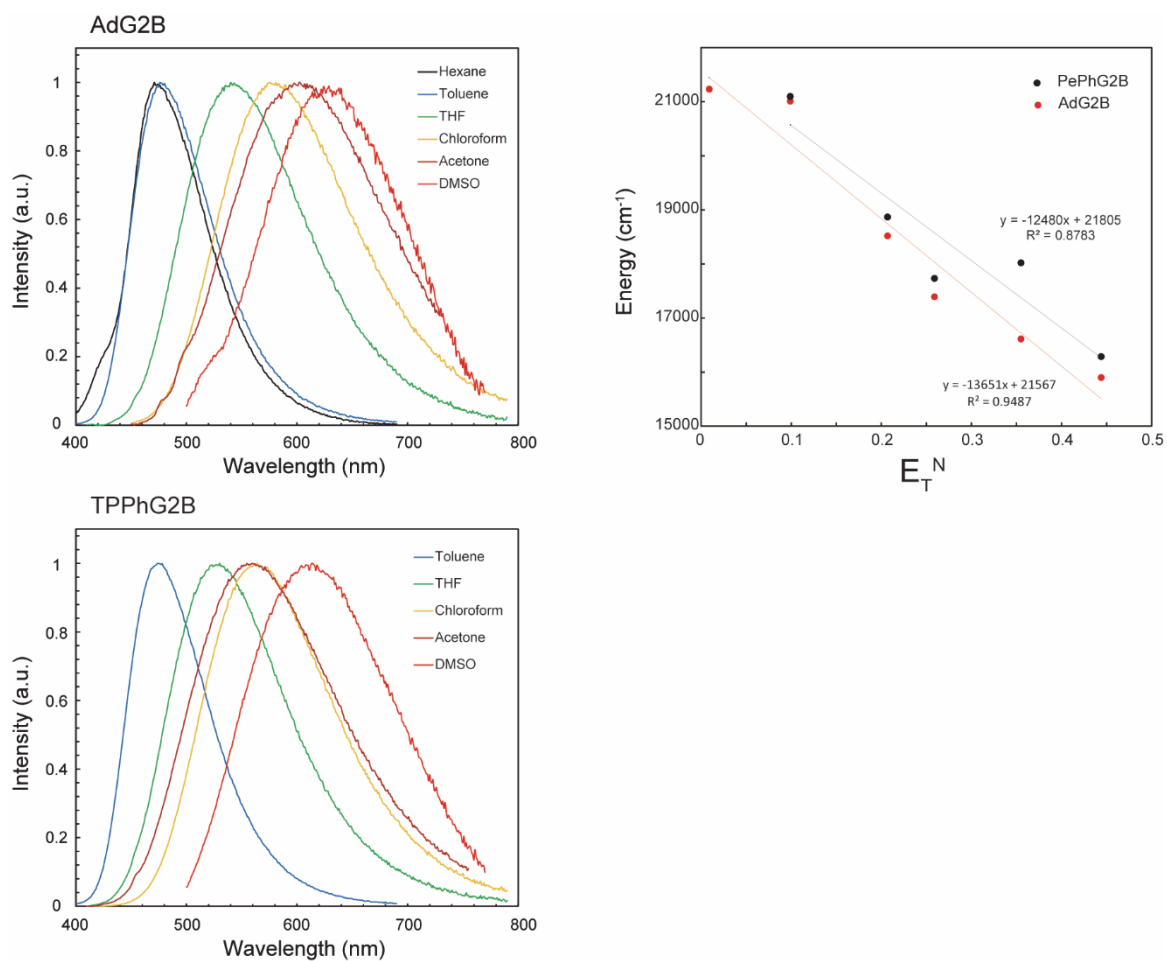


Figure S5. PL spectra of dendrimers in various solvents, and Lippert-Mataga plot.



Figure S6. Photograph of AdG2B solution under UV irradiation. From left: hexane, toluene, THF, chloroform, acetone, and DMSO.



**Figure S7.** Photograph of TPPhG2B solution under UV irradiation. From left: hexane, toluene, THF, chloroform, acetone, and DMSO.

**Table S2.** PL data of AdG2B in various solvents.

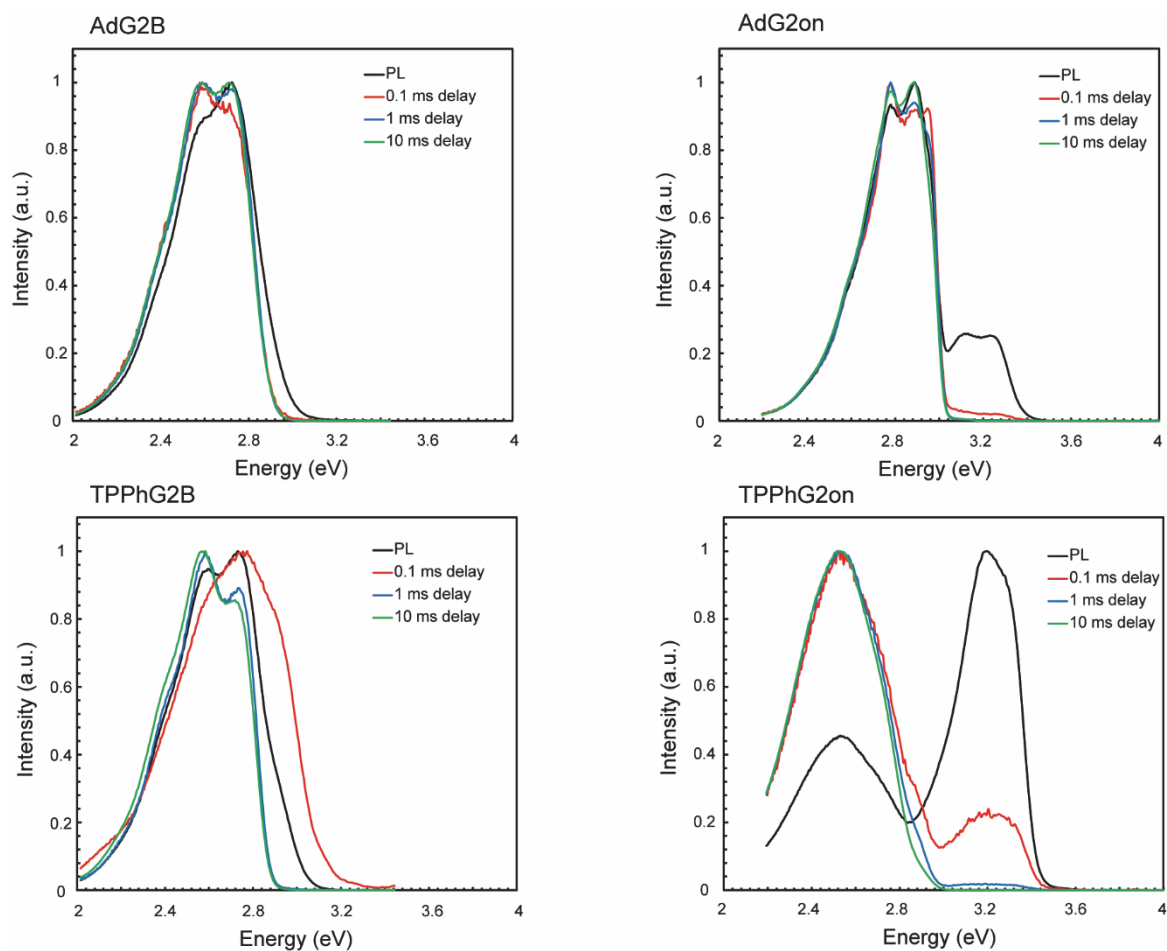
Compound	Hexane	Toluene	THF	Chloroform	Acetone	DMSO
Concentration ( $\mu\text{M}$ )	Sat. <sup>a)</sup>	8.4	8.4	8.4	Sat. <sup>a)</sup>	Sat. <sup>a)</sup>
PL $\lambda_{\text{max}}$ (nm)	471	476	540	575	602	629
PLQY (%)	29 <sup>b)</sup>	66 <sup>c)</sup>	41 <sup>b)</sup>	19 <sup>b)</sup>	-	-

a) Saturated solution was prepared by sonication and filtration through a 0.2  $\mu\text{M}$  pore size syringe filter. b) Excited at 300 nm. c) Excited at 350 nm.

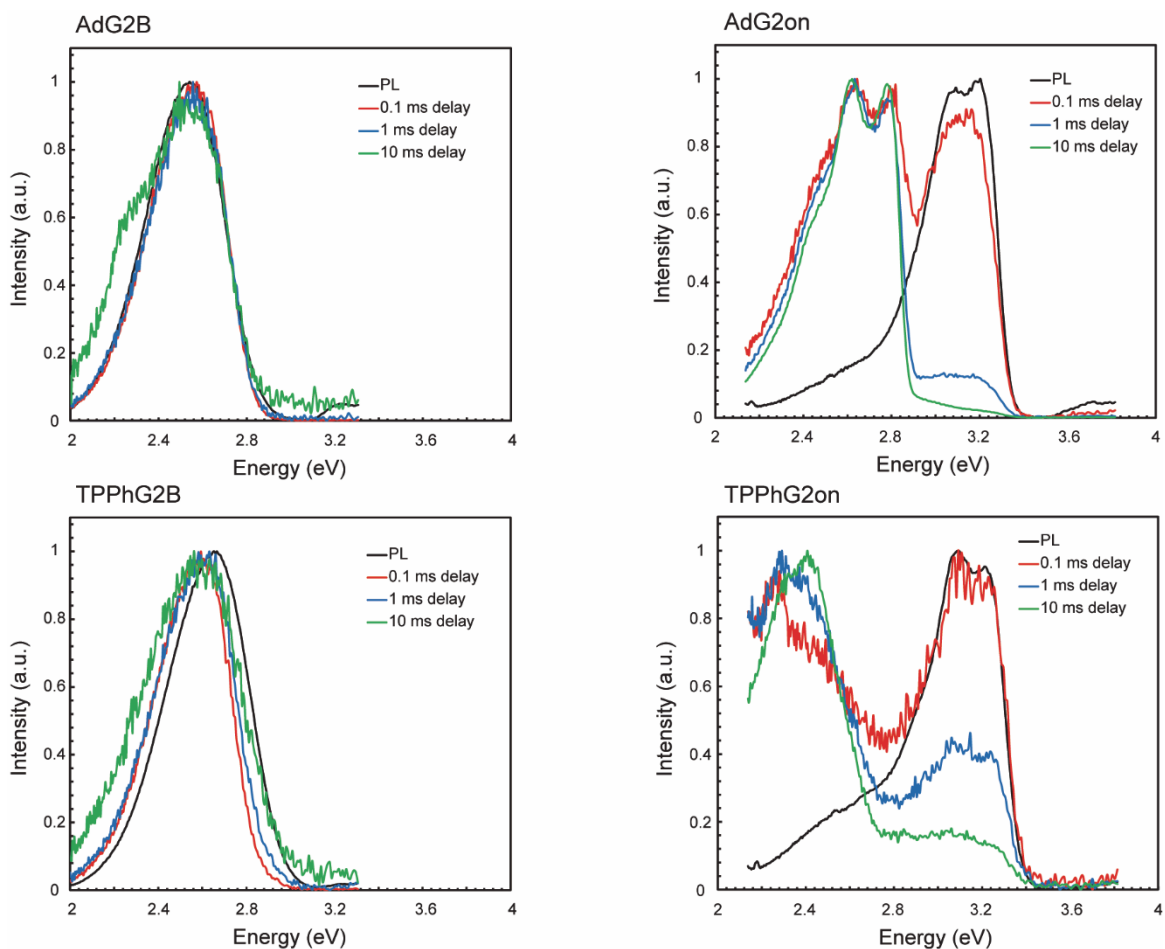
**Table S3.** PL data of TPPhG2B in various solvents.

Compound	Hexane	Toluene	THF	Chloroform	Acetone	DMSO
Concentration ( $\mu\text{M}$ )	Sat. <sup>a)</sup>	8.4	8.4	8.4	Sat. <sup>a)</sup>	8.4
PL $\lambda_{\text{max}}$ (nm)	-	474	530	564	555	614
PLQY (%)	-	43 <sup>c)</sup>	50 <sup>b)</sup>	38 <sup>b)</sup>	15 <sup>c)</sup>	6 <sup>b)</sup>

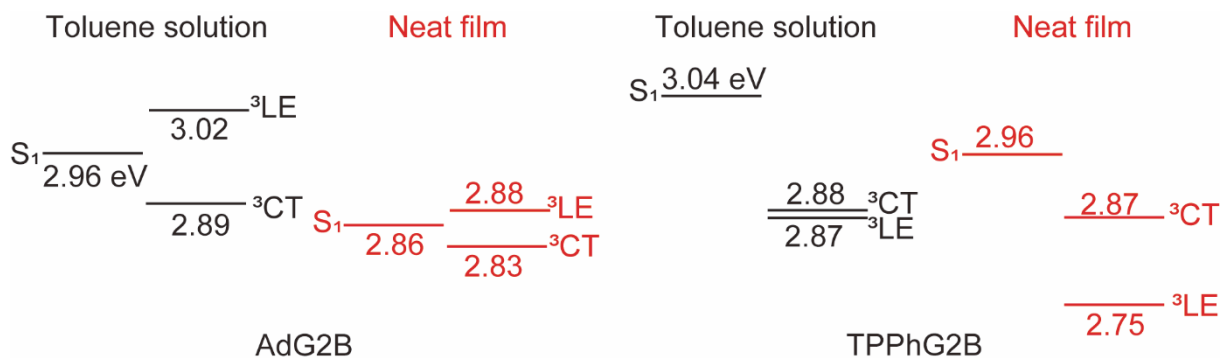
a) Saturated solution was prepared by sonication and filtration through a 0.2  $\mu\text{M}$  pore size syringe filter. b) Excited at 300 nm. c) Excited at 350 nm.



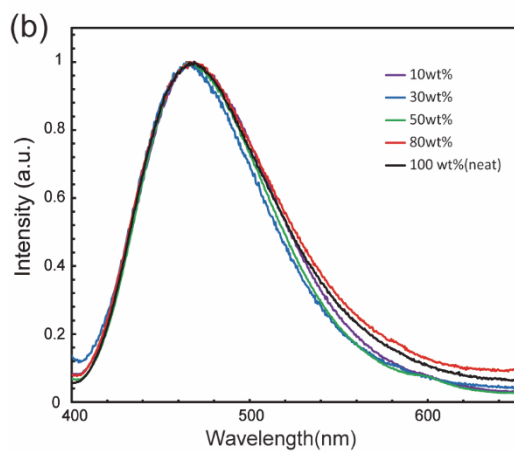
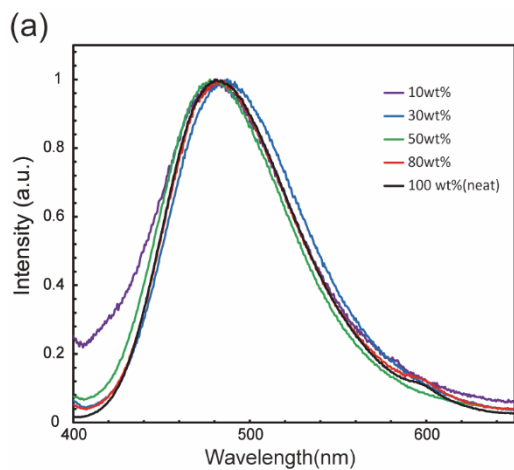
**Figure S8.** Steady-state PL and phosphorescence spectra of AdG2B, TPPhG2B, AdG2on, and TPPhG2on toluene solutions at 77 K.  $S_1$  and  $T_1$  energy of the dendrimers were determined from the onset of the steady-state PL and 10 ms delay phosphorescence spectra. The  $T_1$  ( $^3LE$ ) level of the dendrons was determined from the onset of the 10 ms delay phosphorescence spectra.



**Figure S9.** Steady-state PL and phosphorescence spectra of AdG2B, TPPhG2B, AdG2on, and TPPhG2on neat film at 77 K.  $S_1$  and  $T_1$  energy of the dendrimers were determined from the onset of the steady-state PL and 0.1 ms delay phosphorescence spectra. The  $T_1$  ( $^3LE$ ) level of the dendrons was determined from the onset of the 10 ms delay phosphorescence spectra.



**Figure S10** Energy diagram of excited states of AdG2B and TPPhG2B in toluene solution and neat film. The energy levels are based on Table 2 in the main text.



**Figure S11** PL spectra of dendrimer doped PMMA film spin-coated from chloroform solution measured in vacuum. (a) tBuG2B, and (b) TPPhG2B.

## 7. PL decay

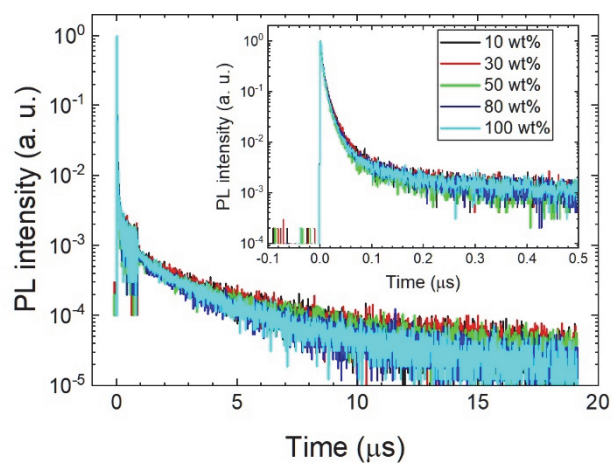


Figure S12 Transient decay spectra of AdG2B doped in PMMA film measured at 300 K.

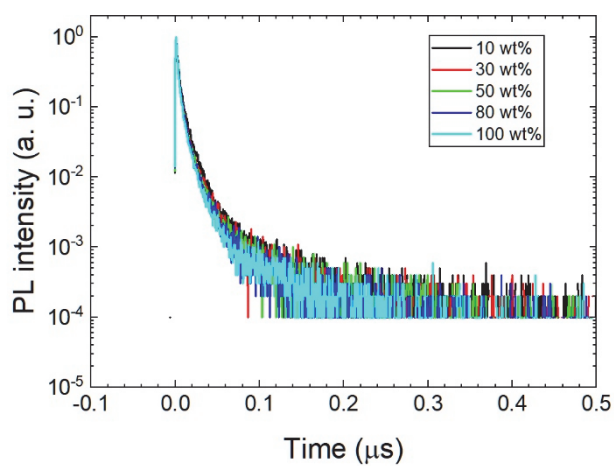
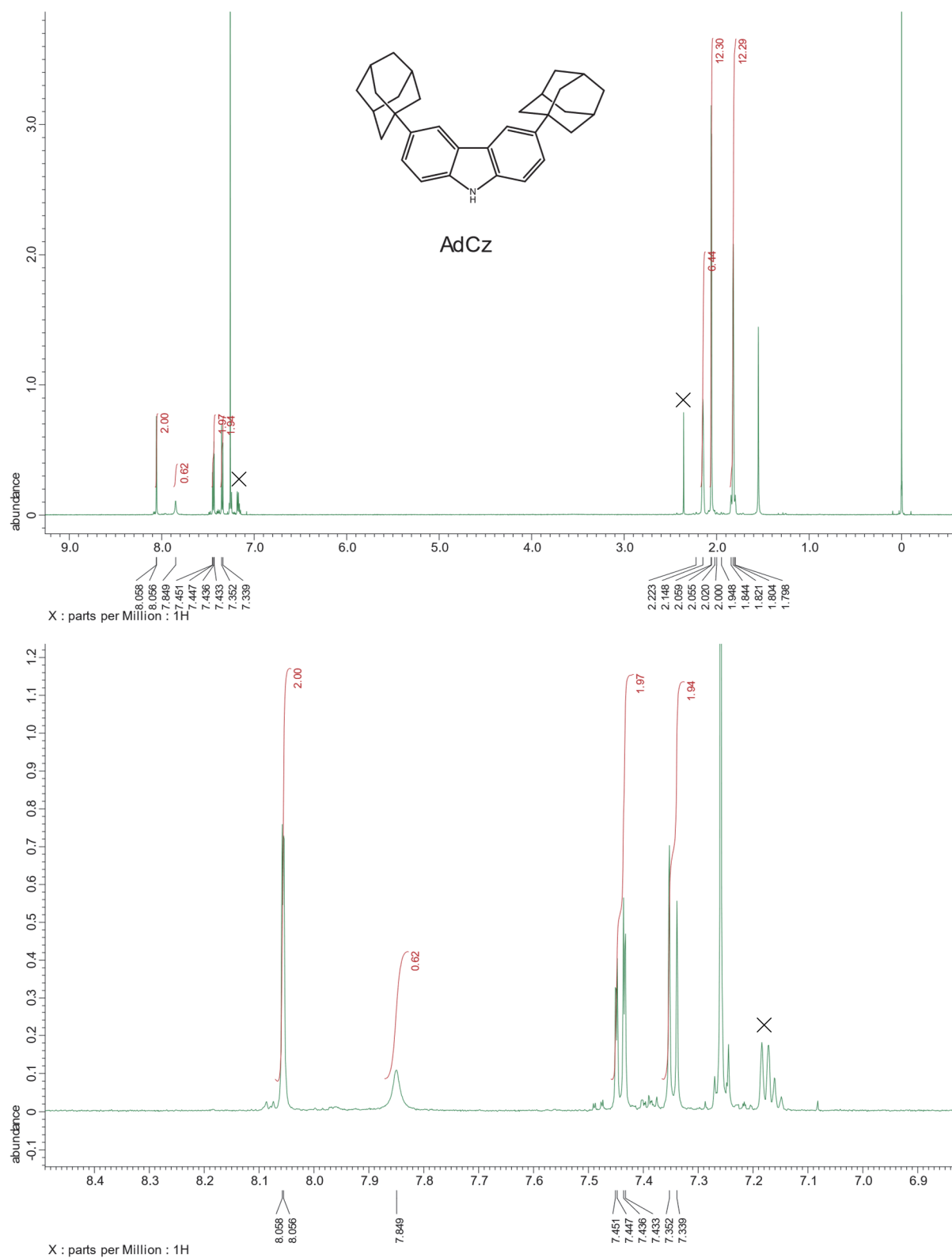


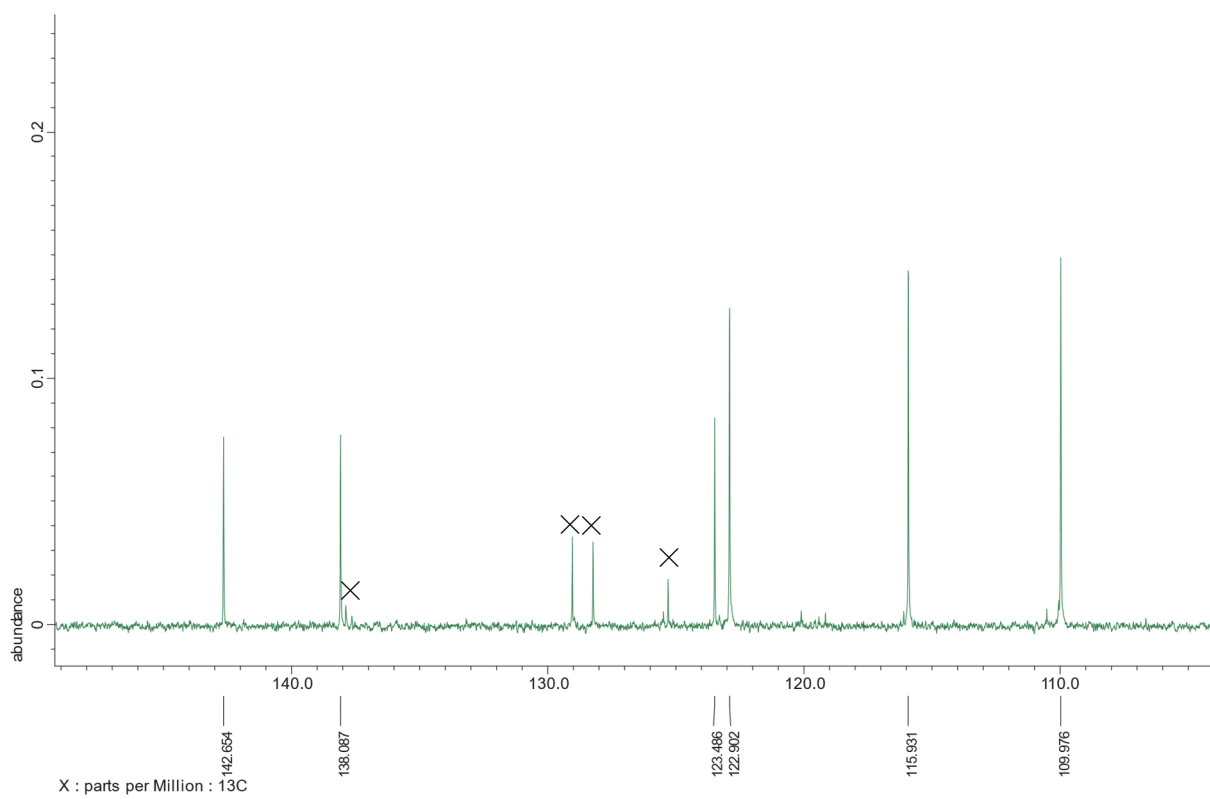
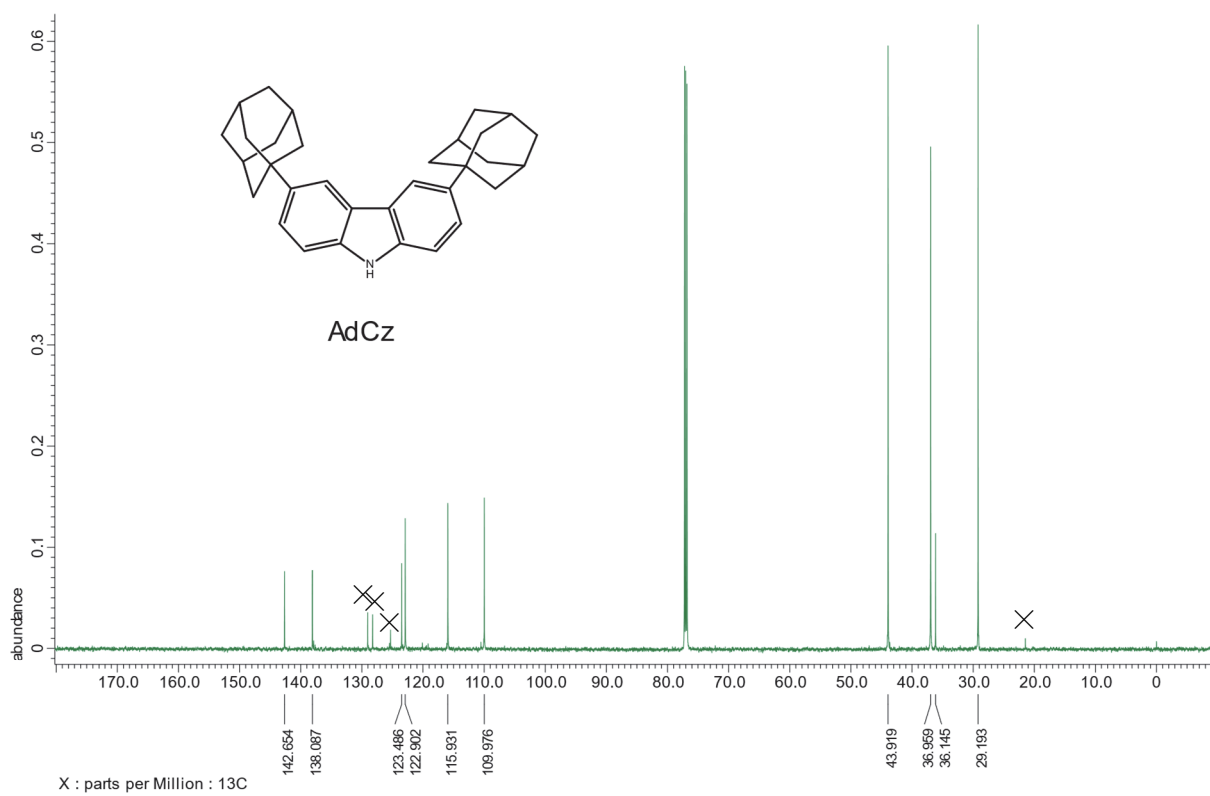
Figure S13 Transient decay spectra of TPPhG2B doped in PMMA film measured at 300 K.

## 8. NMR spectra

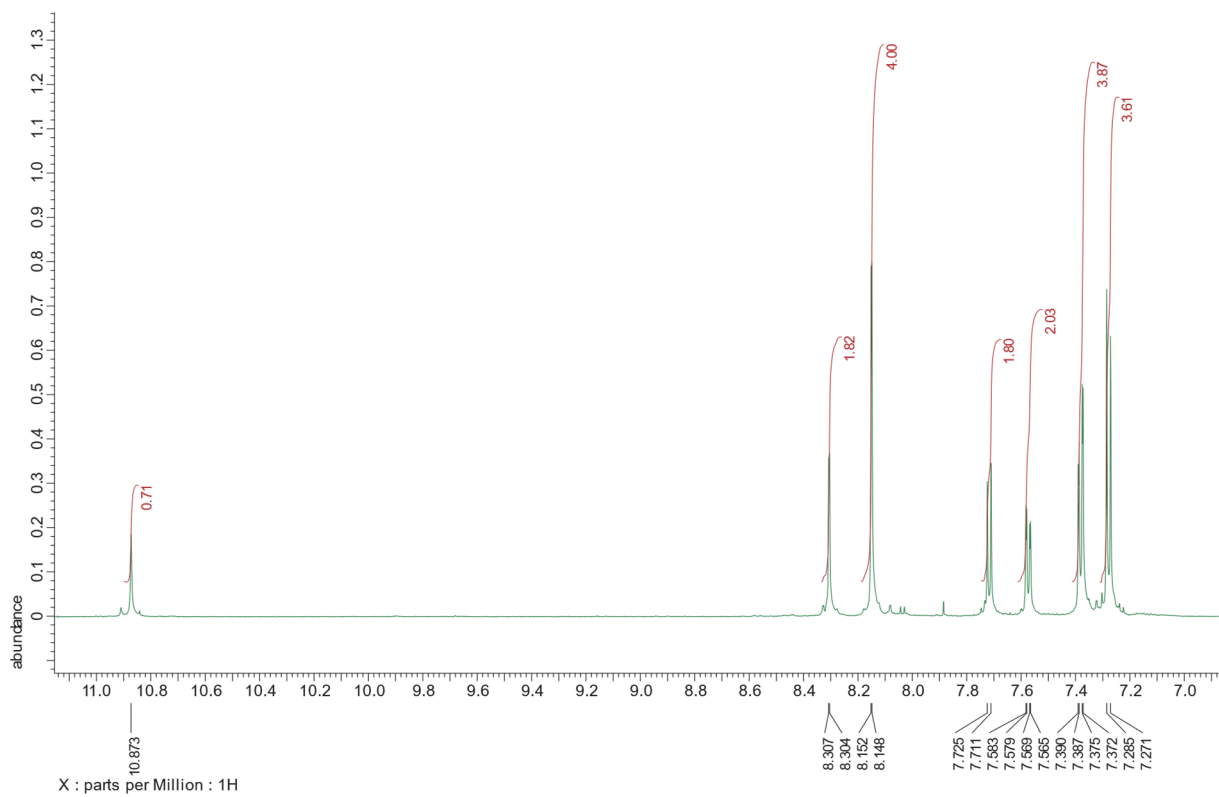
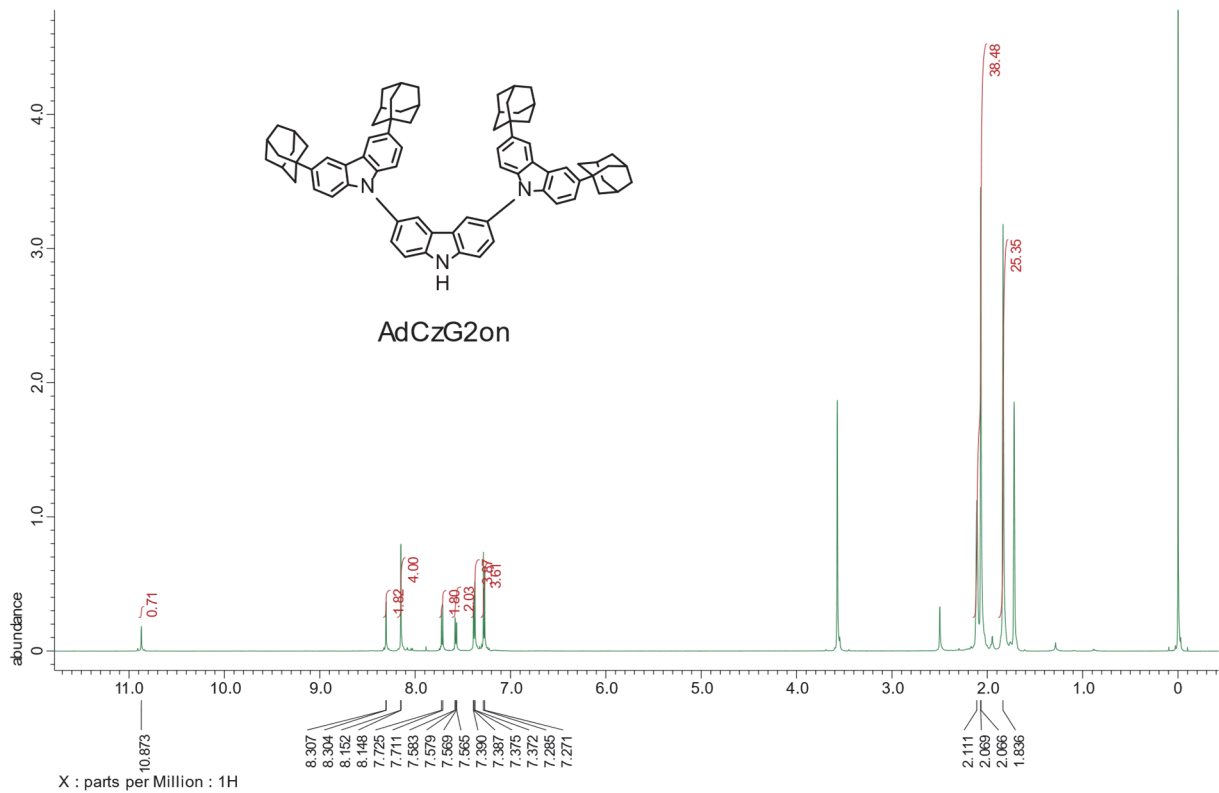


**Figure S14**  $^1\text{H}$  NMR spectrum of AdCz (× peaks are trace amount of toluene).





**Figure S15**  $^{13}\text{C}$  NMR spectrum of AdCz (× peaks are trace amount of toluene).



**Figure S16.**  $^1\text{H}$  NMR spectrum of AdCzG2on.

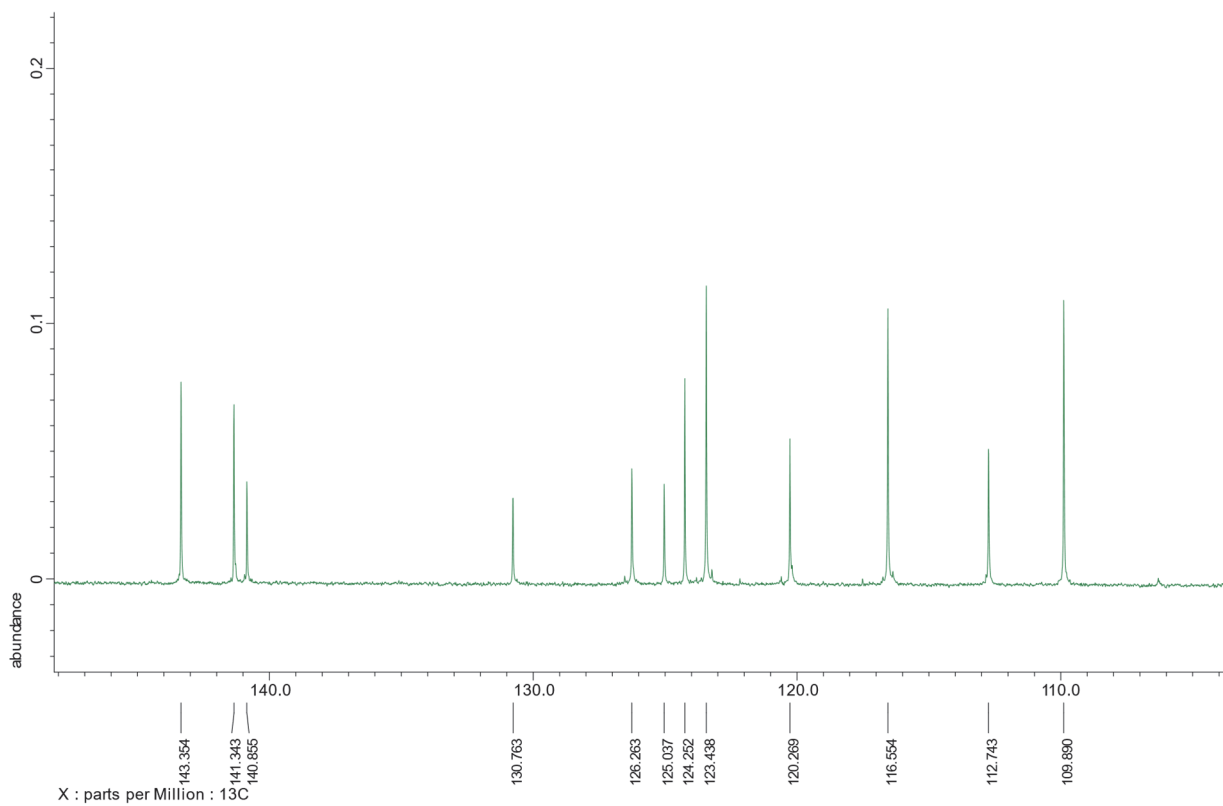
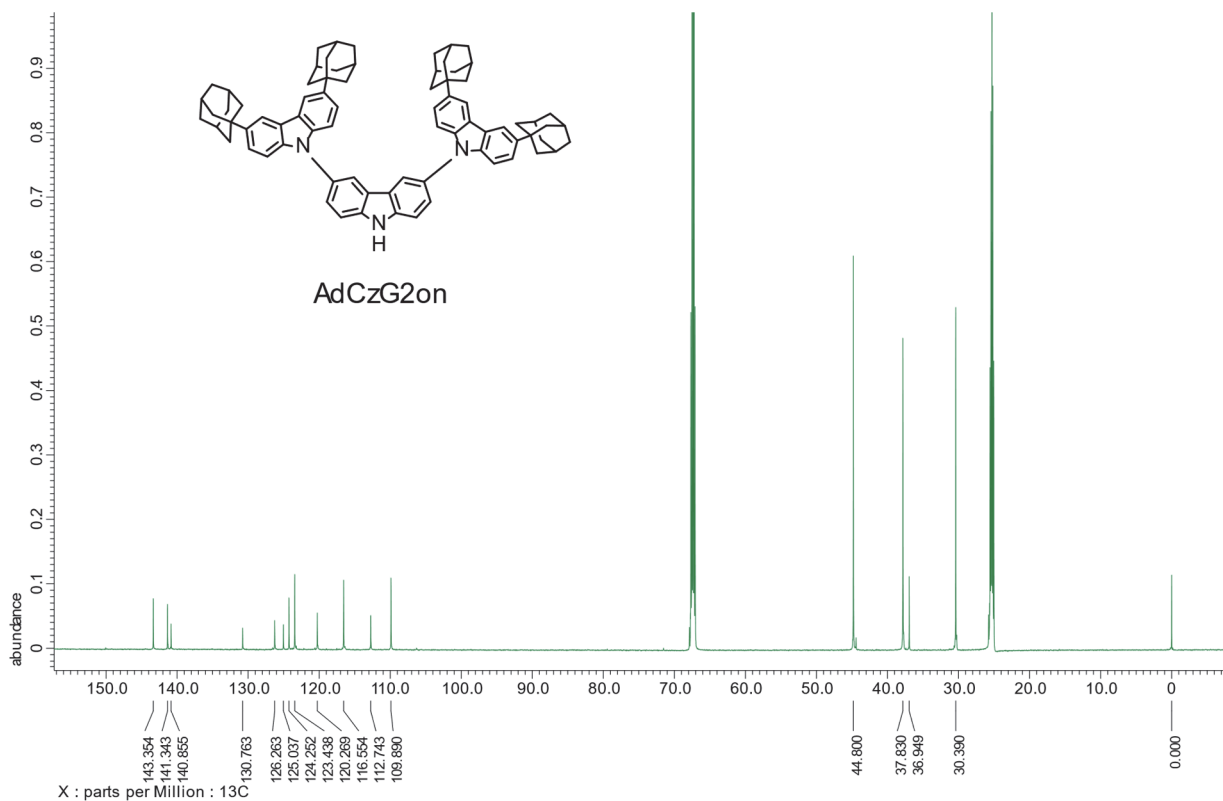


Figure S17  $^{13}\text{C}$  NMR spectrum of AdCzG2on.

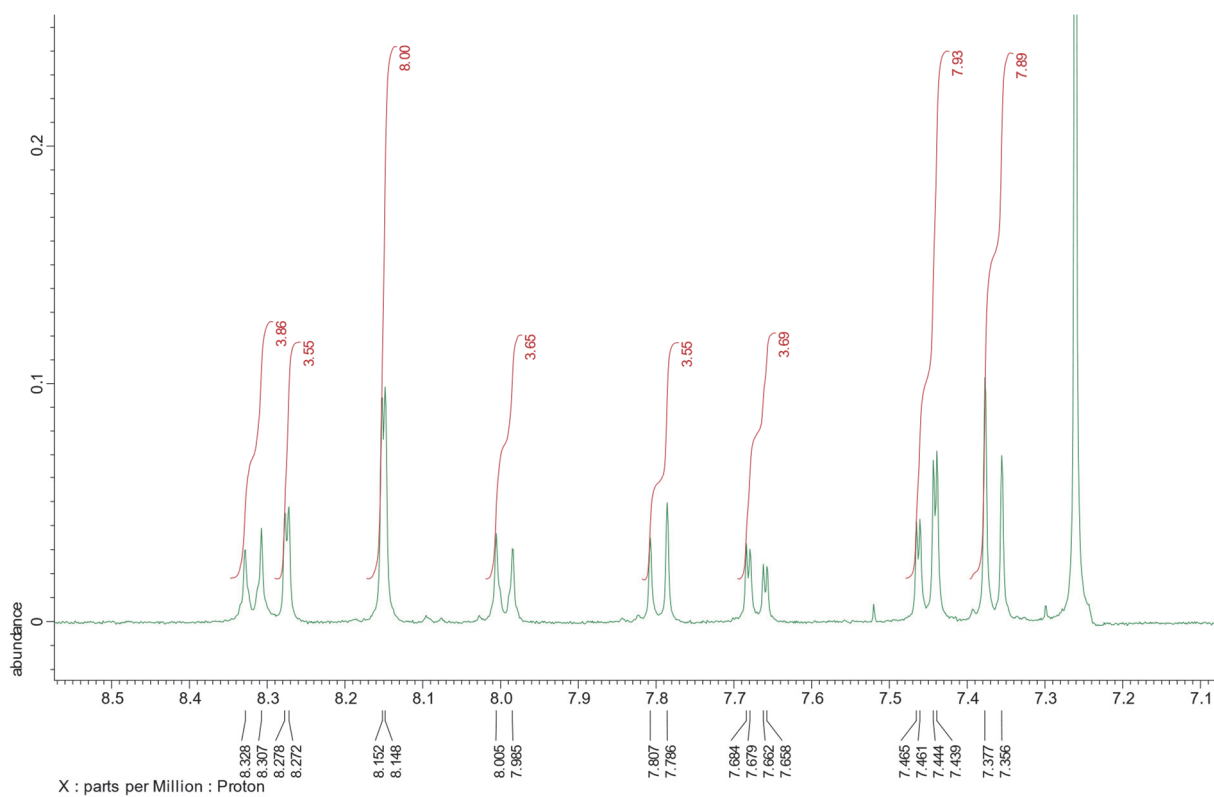
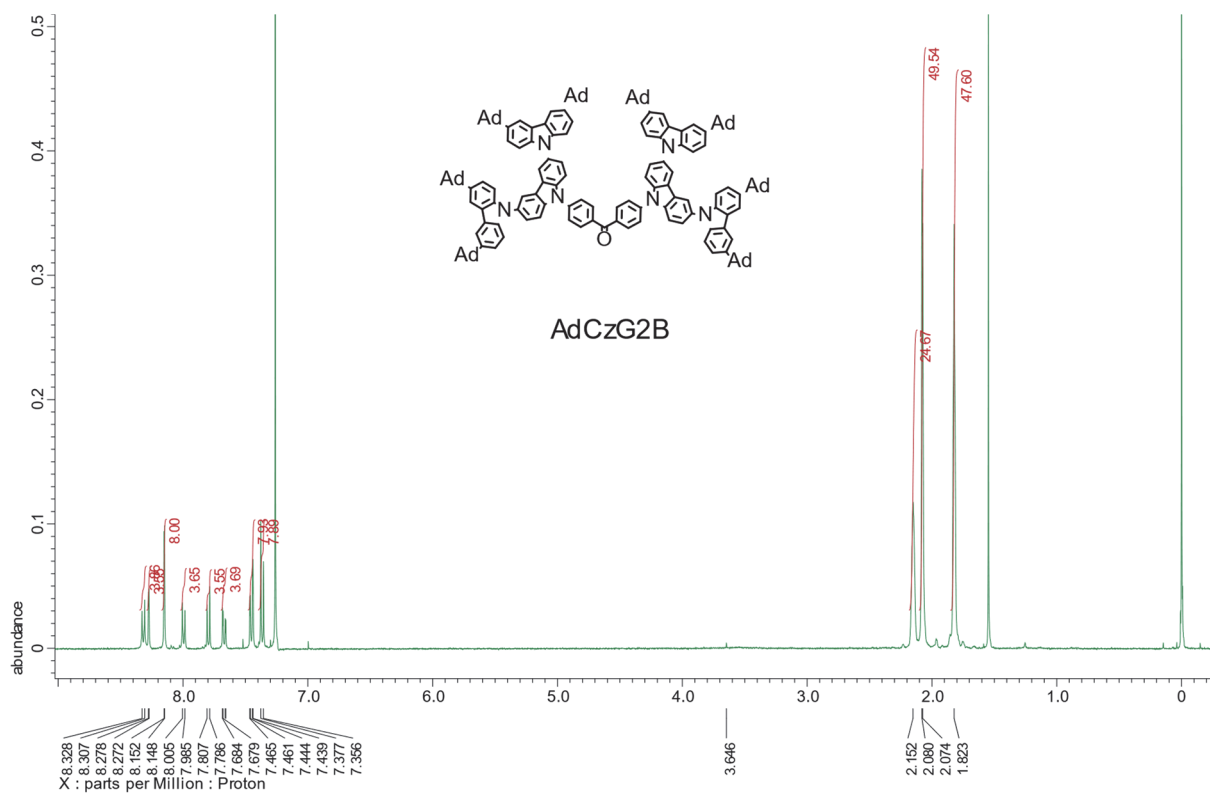


Figure S18  $^1\text{H}$  NMR spectrum of AdCzB.

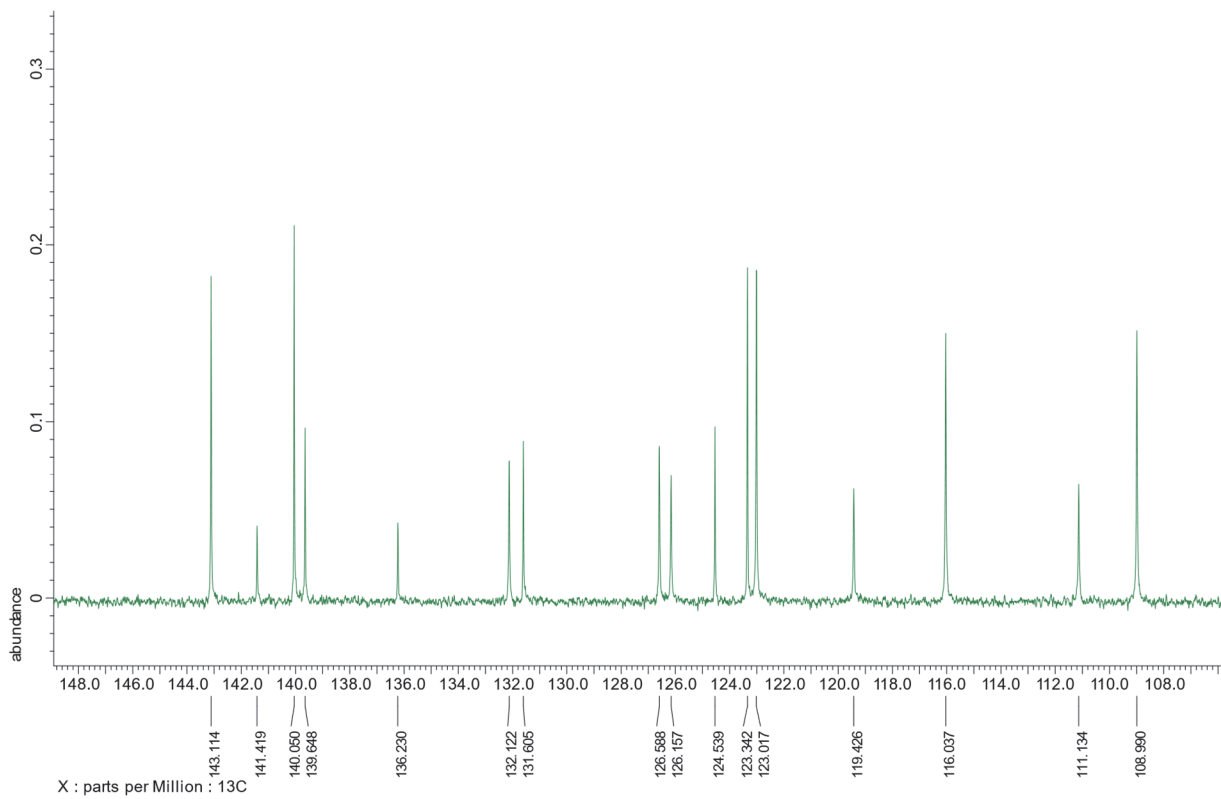
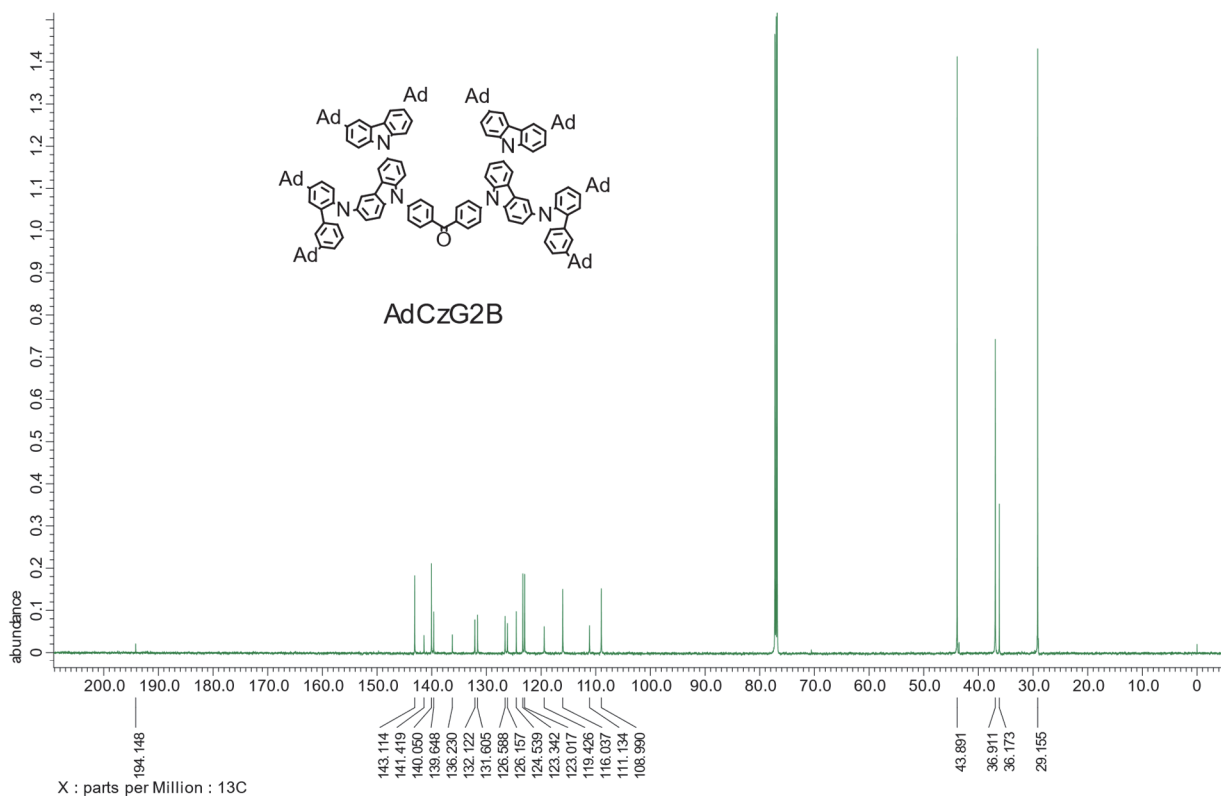


Figure S19 <sup>13</sup>C NMR spectrum of AdCzG2B.

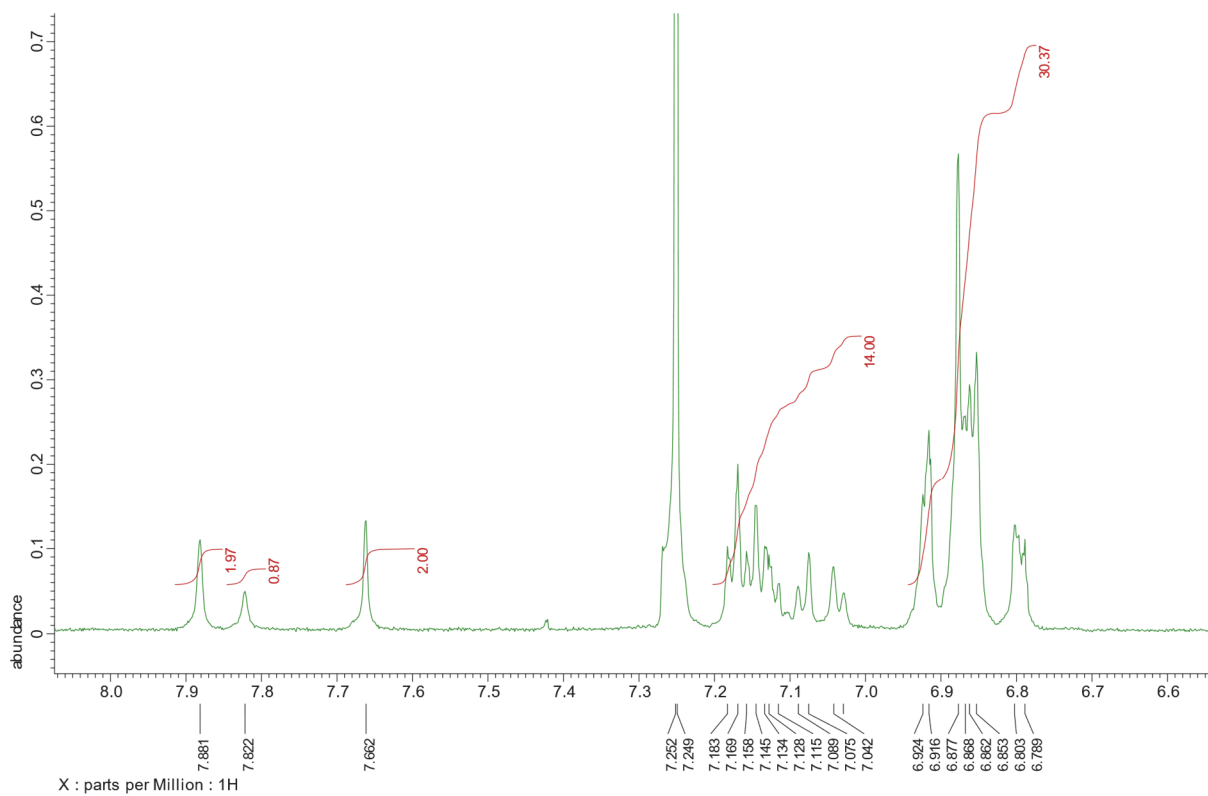
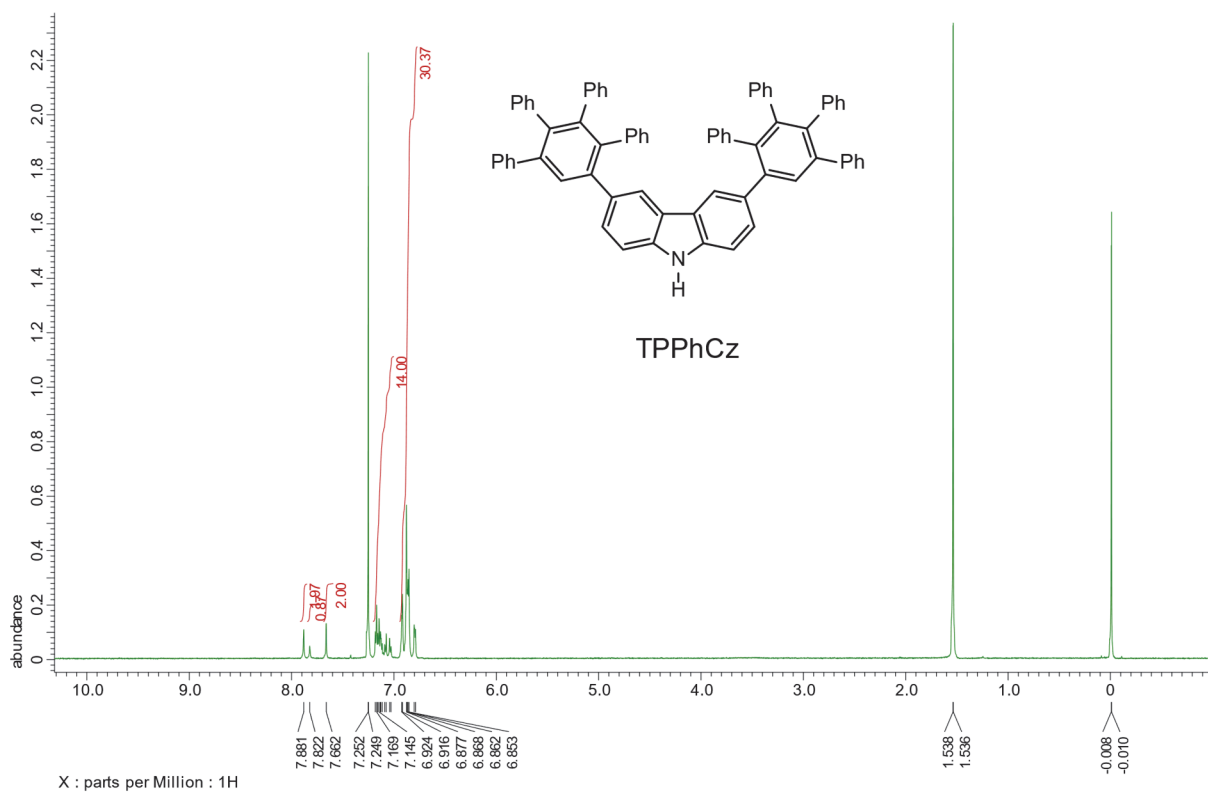


Figure S20  $^1\text{H}$  NMR spectrum of TPPhCz.

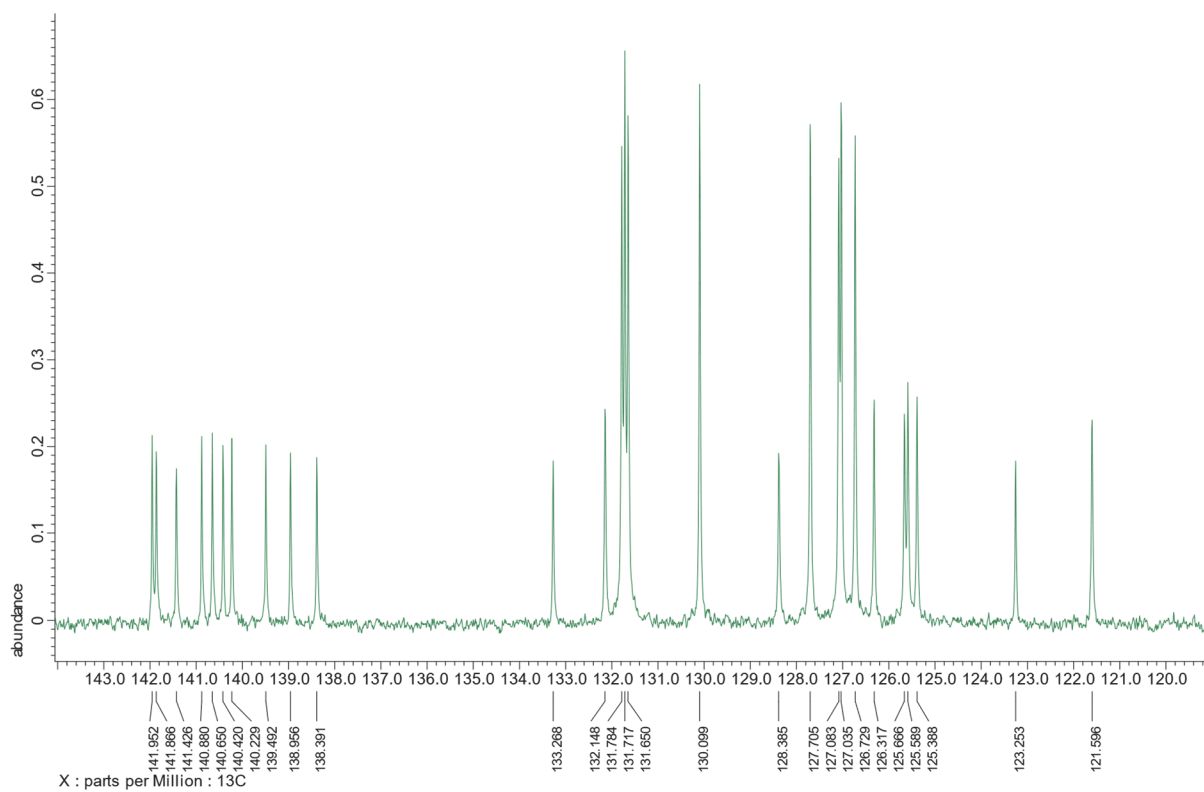
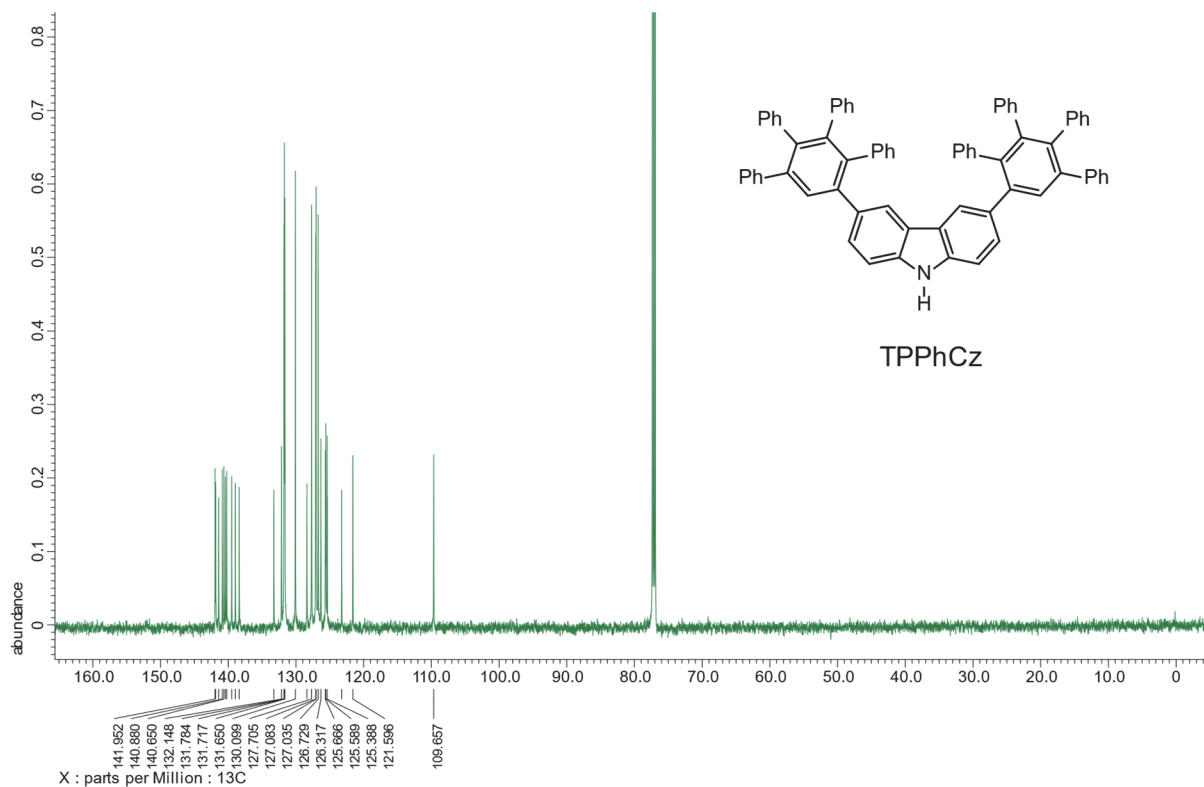


Figure S21 <sup>13</sup>C NMR spectrum of TPPhCz.

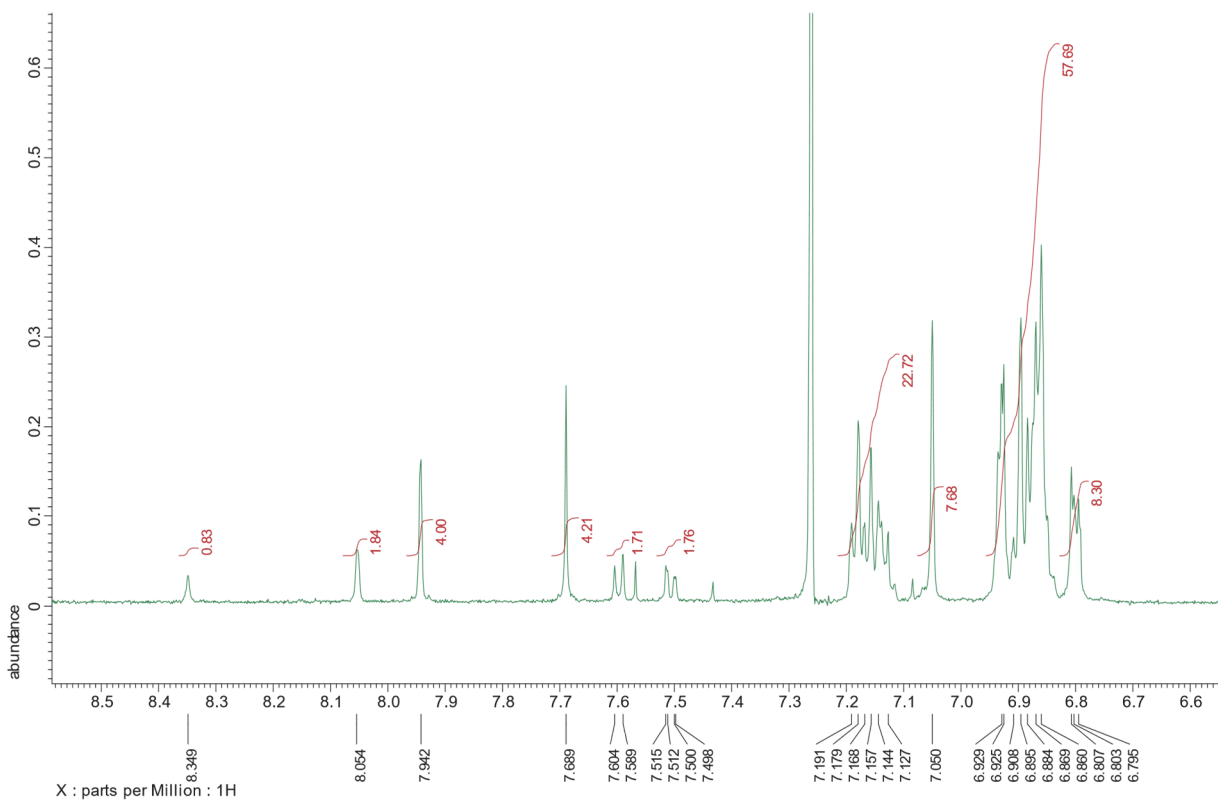
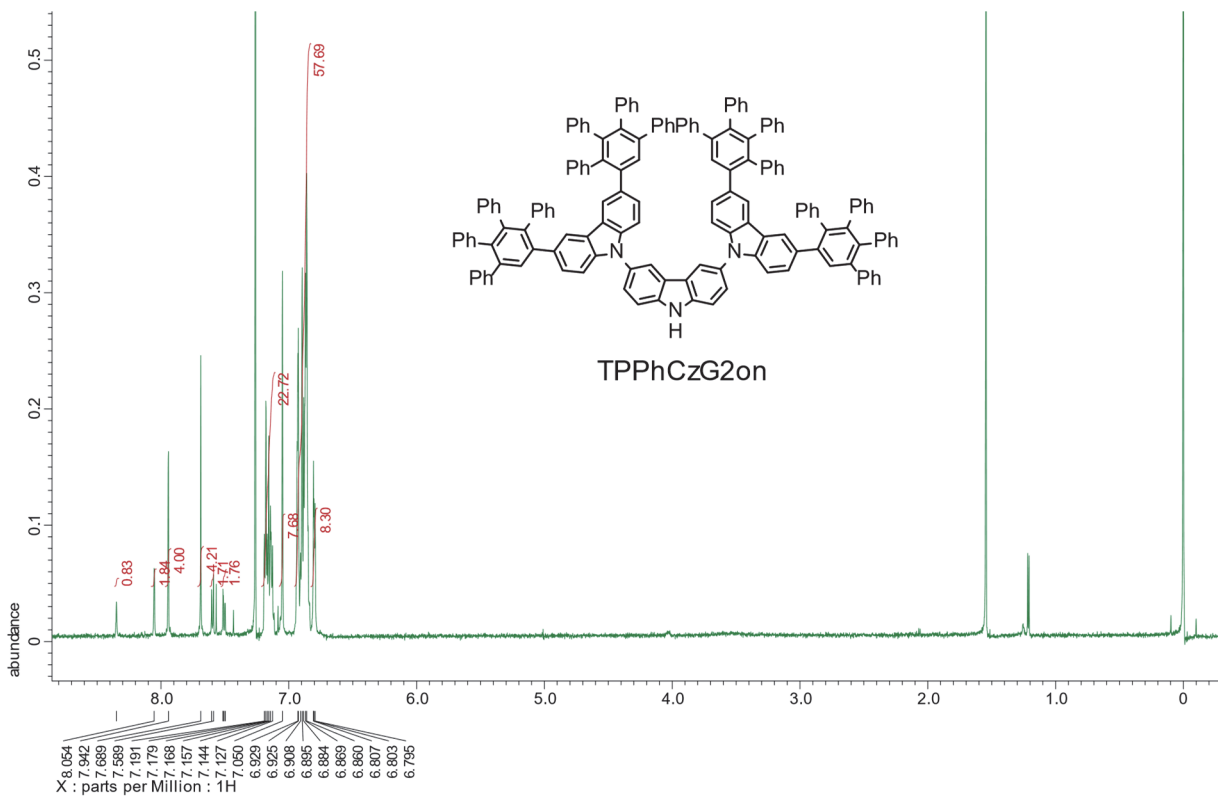




Figure S22 <sup>1</sup>H NMR spectrum of TPPhCzG2on.

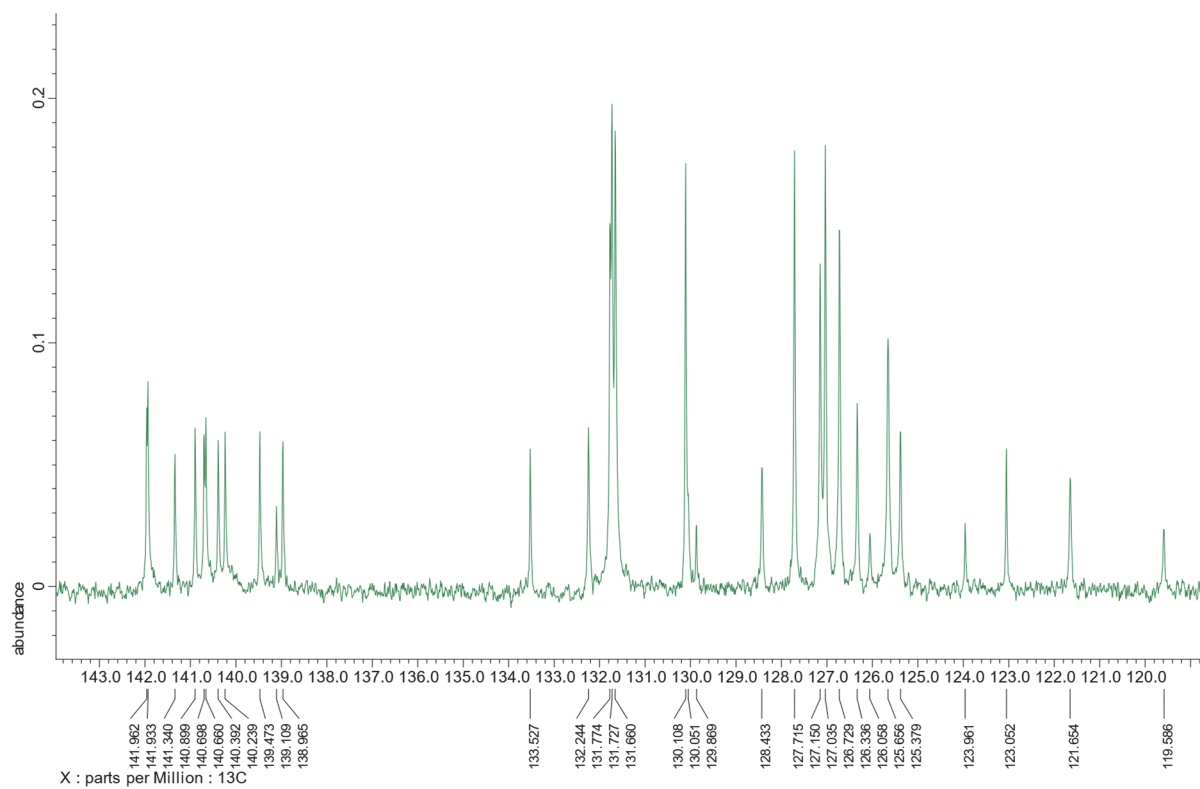
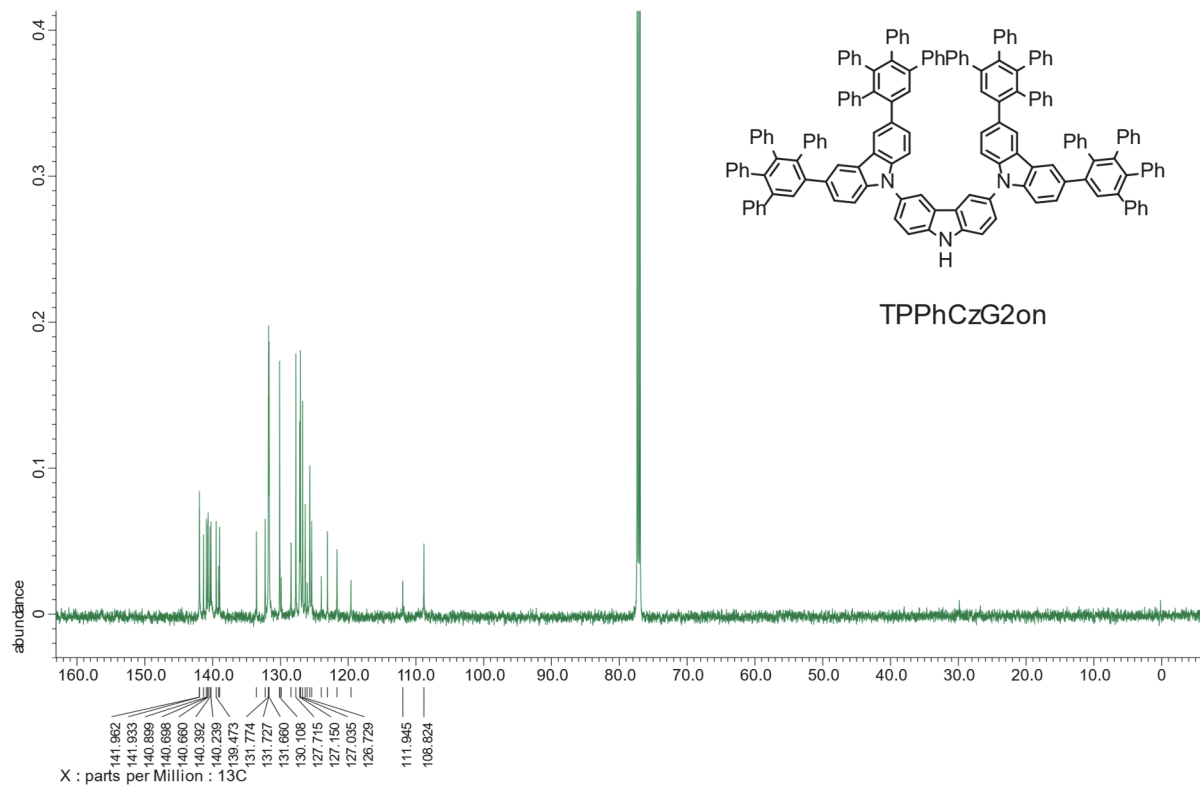


Figure S23 <sup>13</sup>C NMR spectrum of TPPhCzG2on.

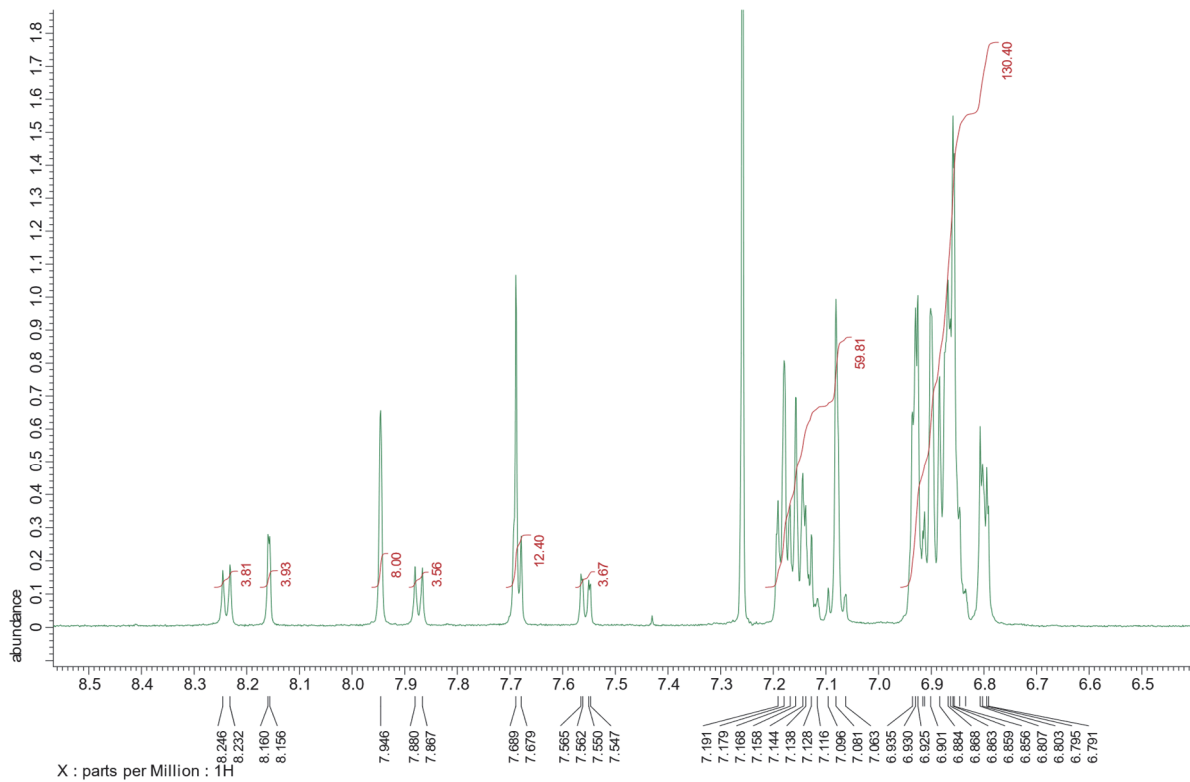
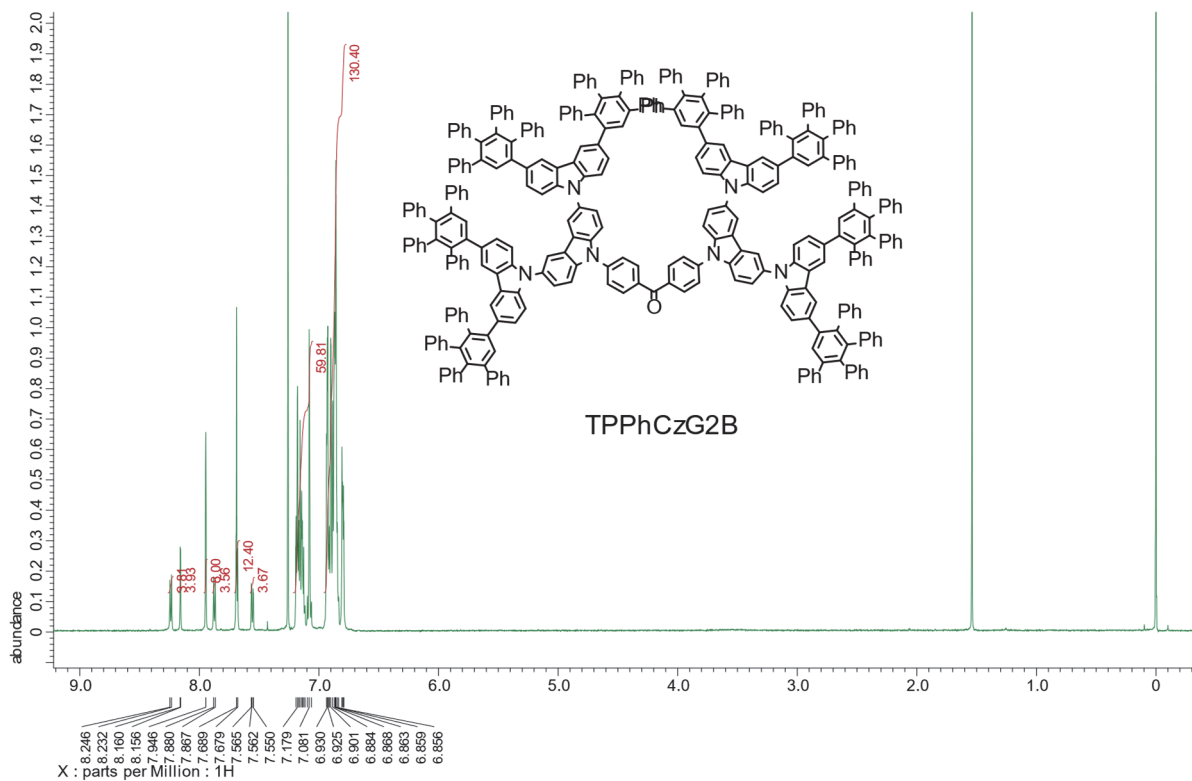


Figure S24  $^1\text{H}$  NMR spectrum of TPPhCzG2B.

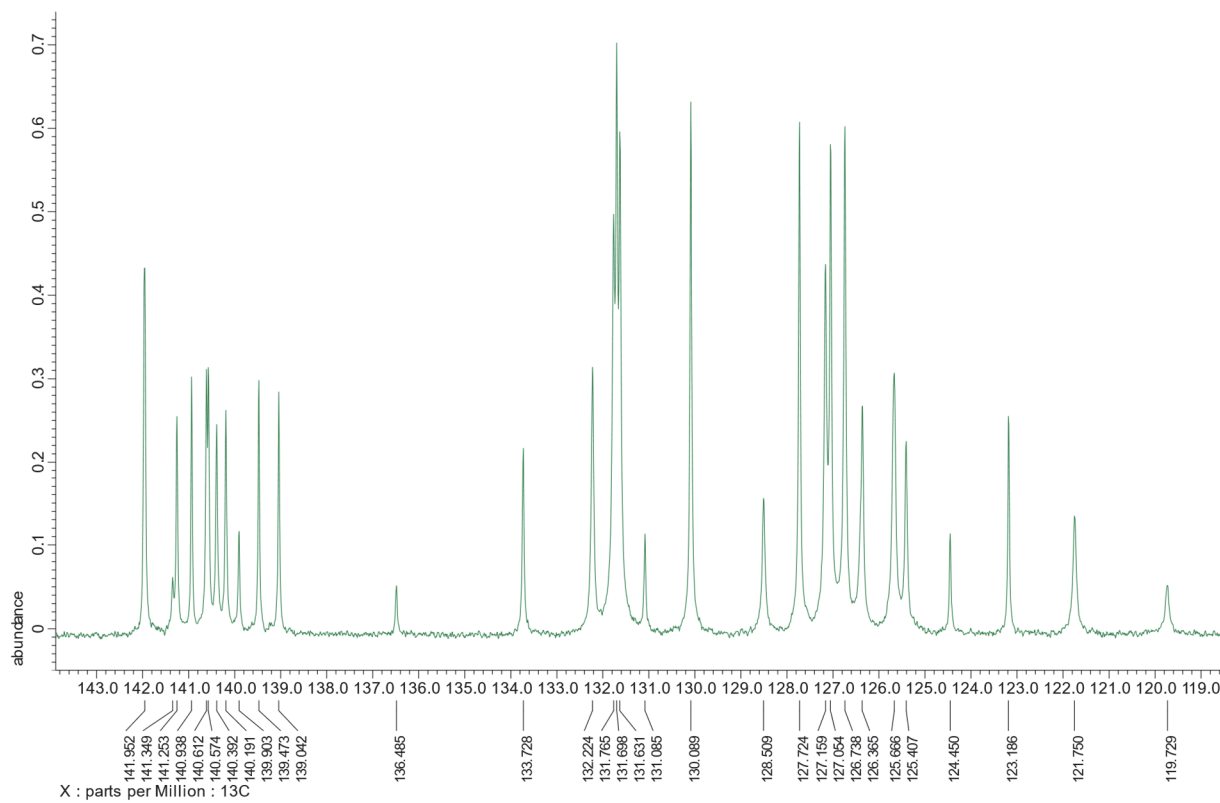
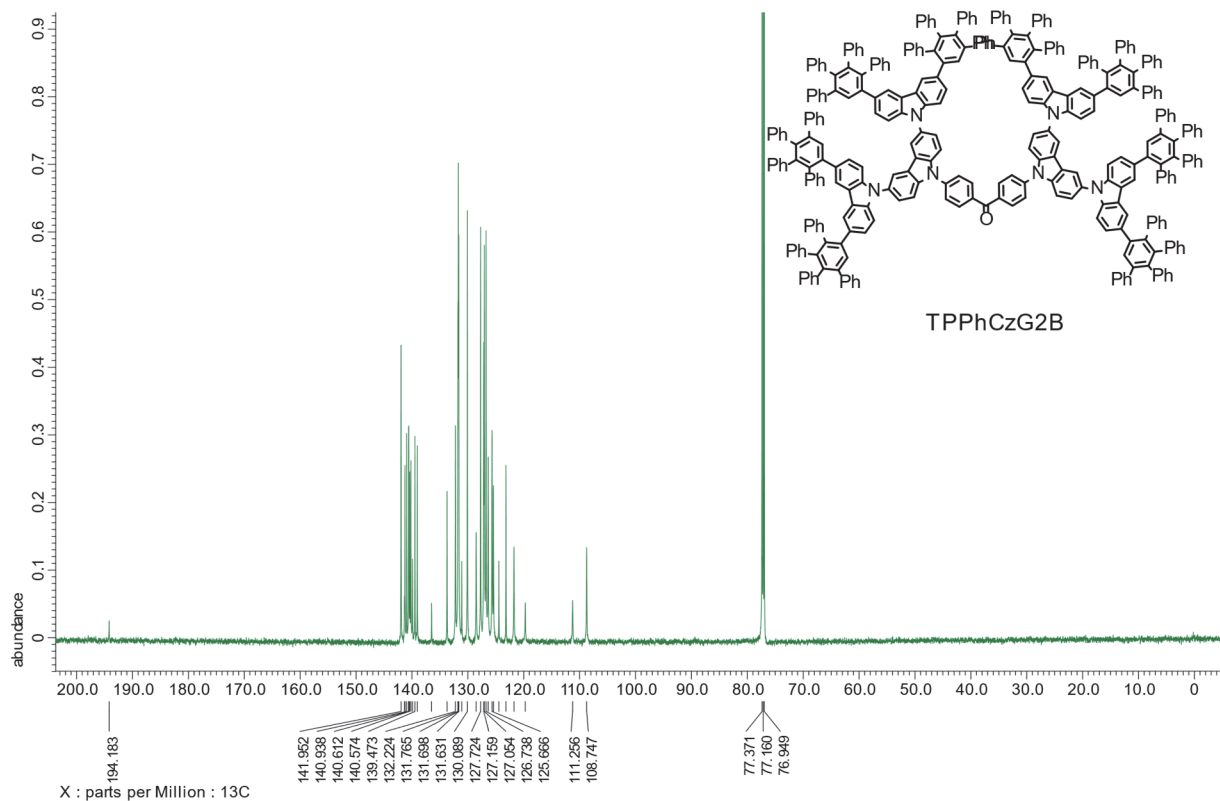


Figure S25  $^{13}\text{C}$  NMR spectrum of TPPhCzG2B.

## 9. MALDI TOF-MS spectra

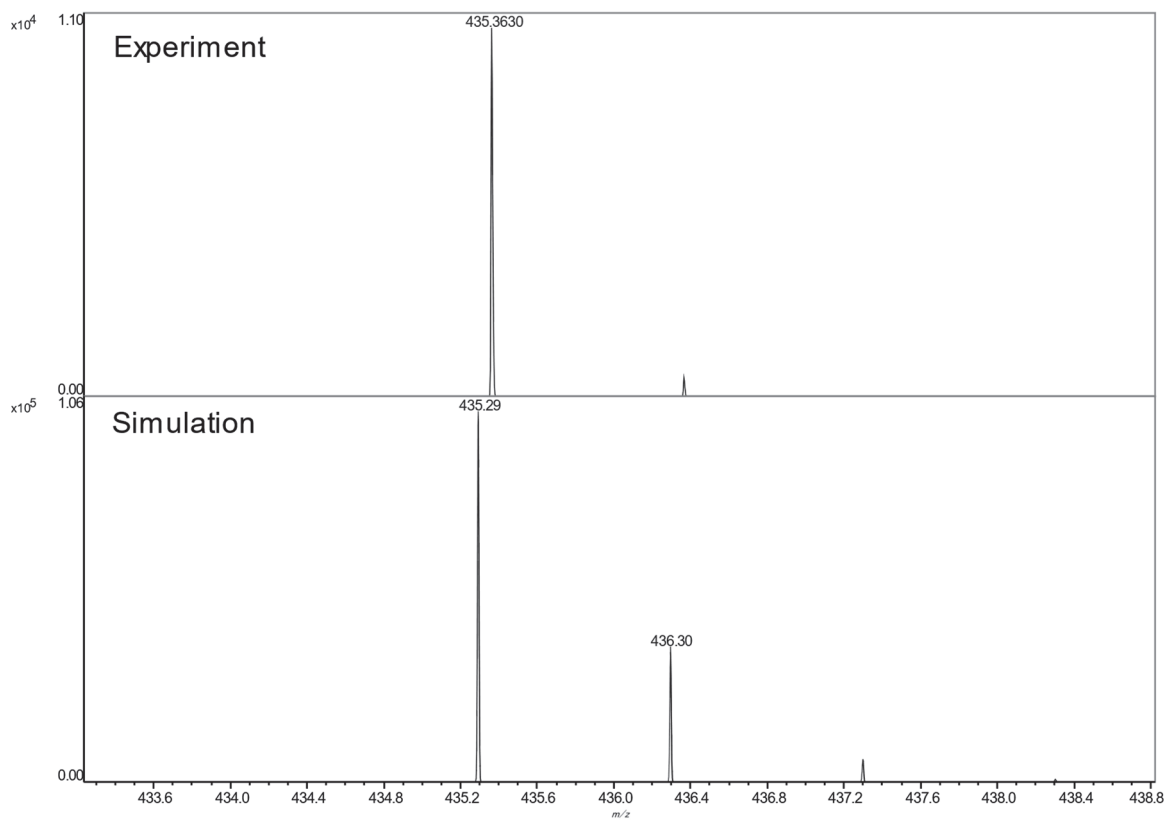
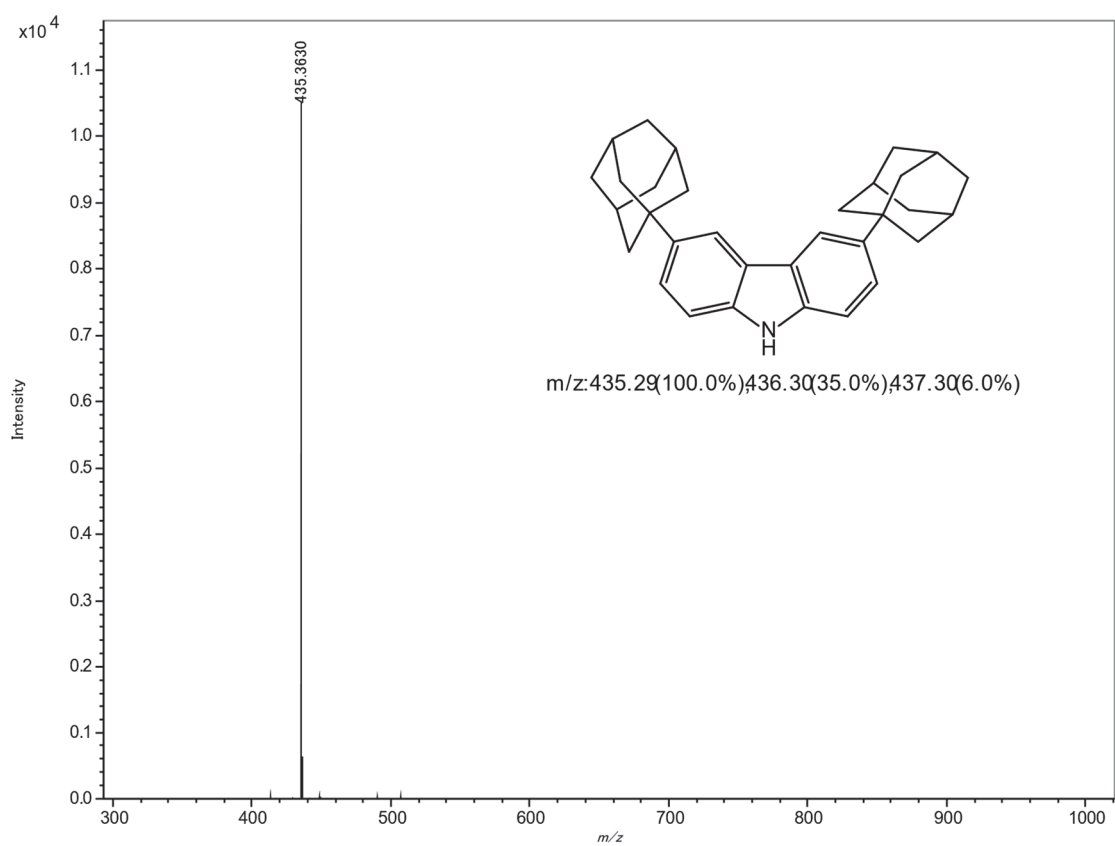
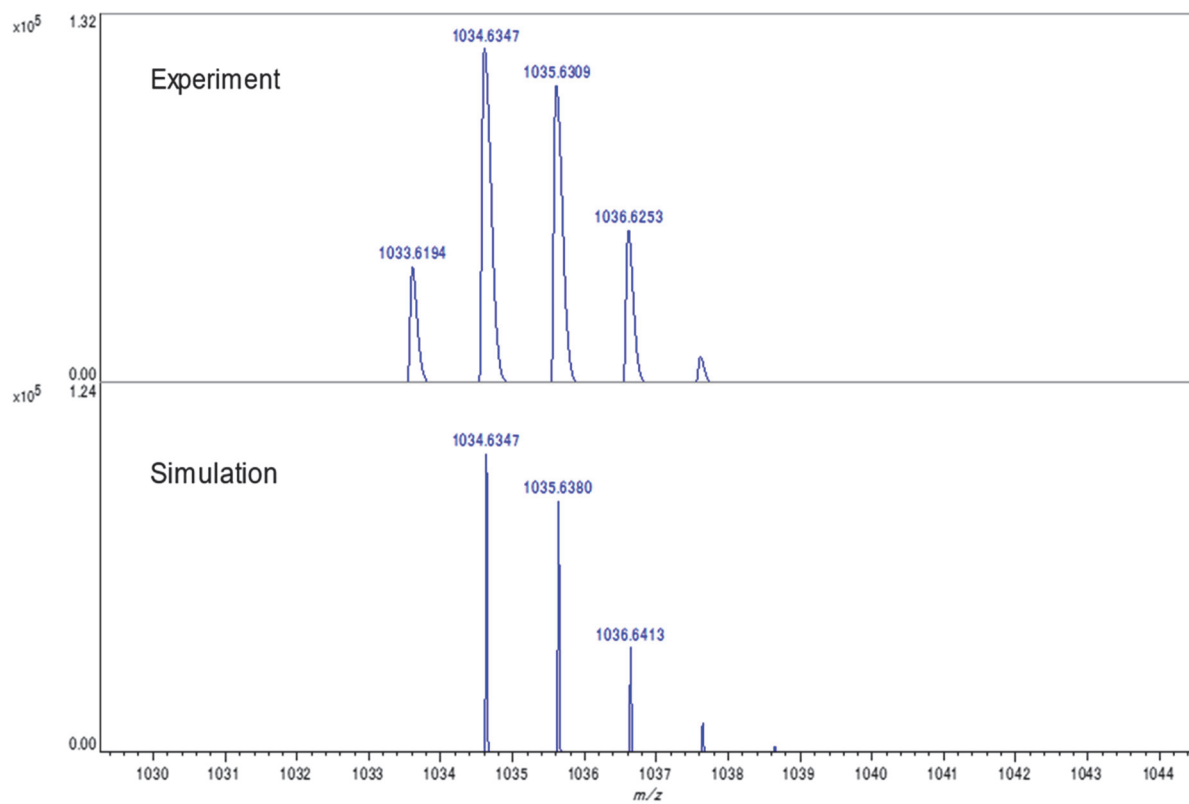
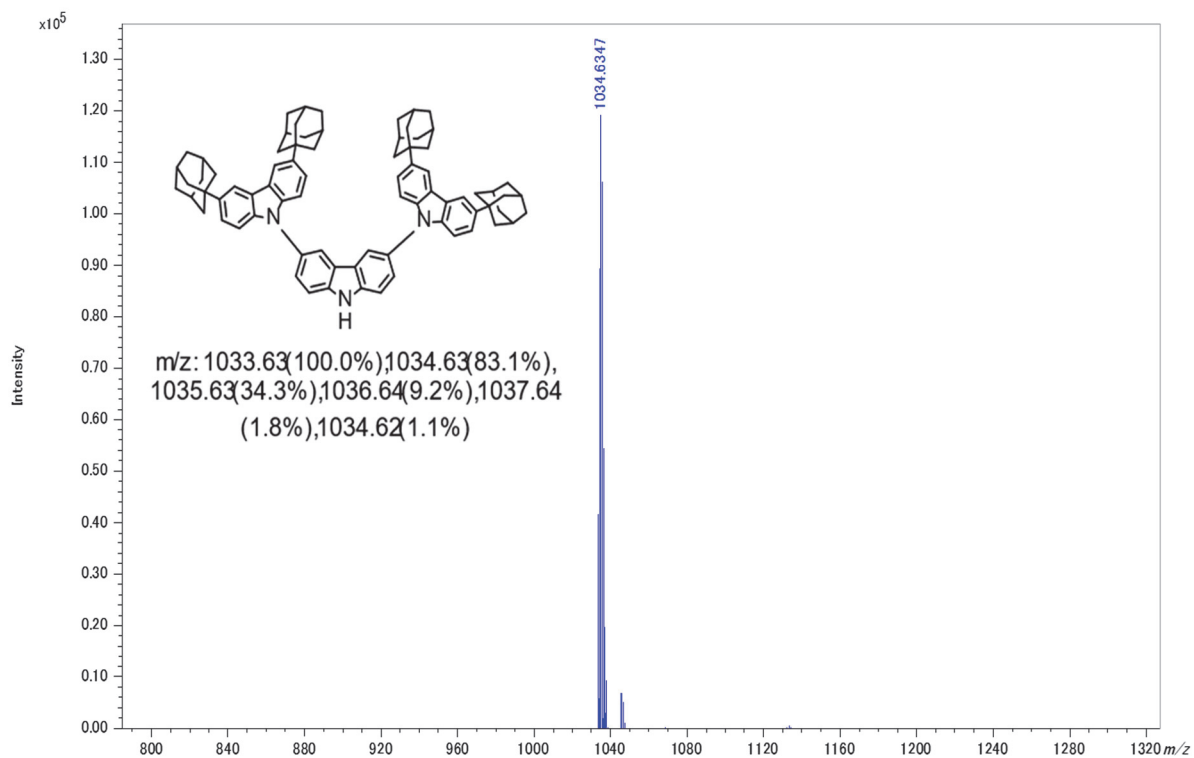
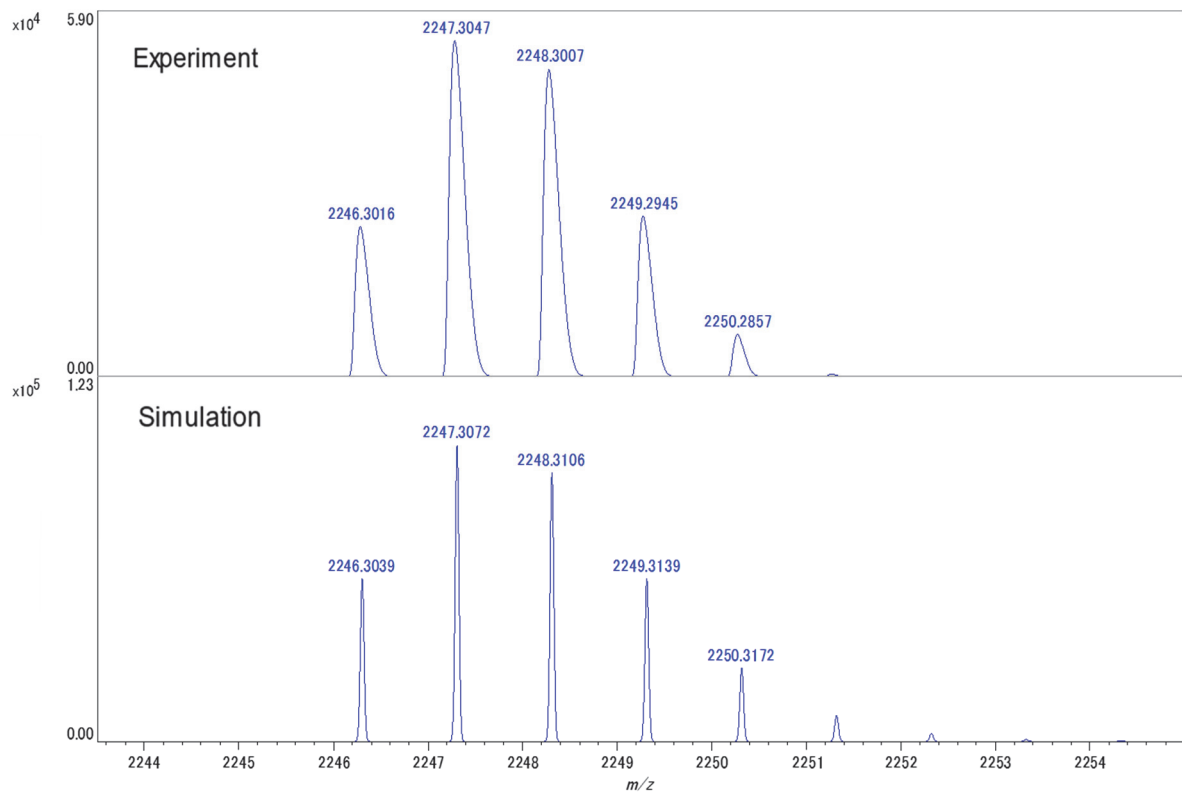
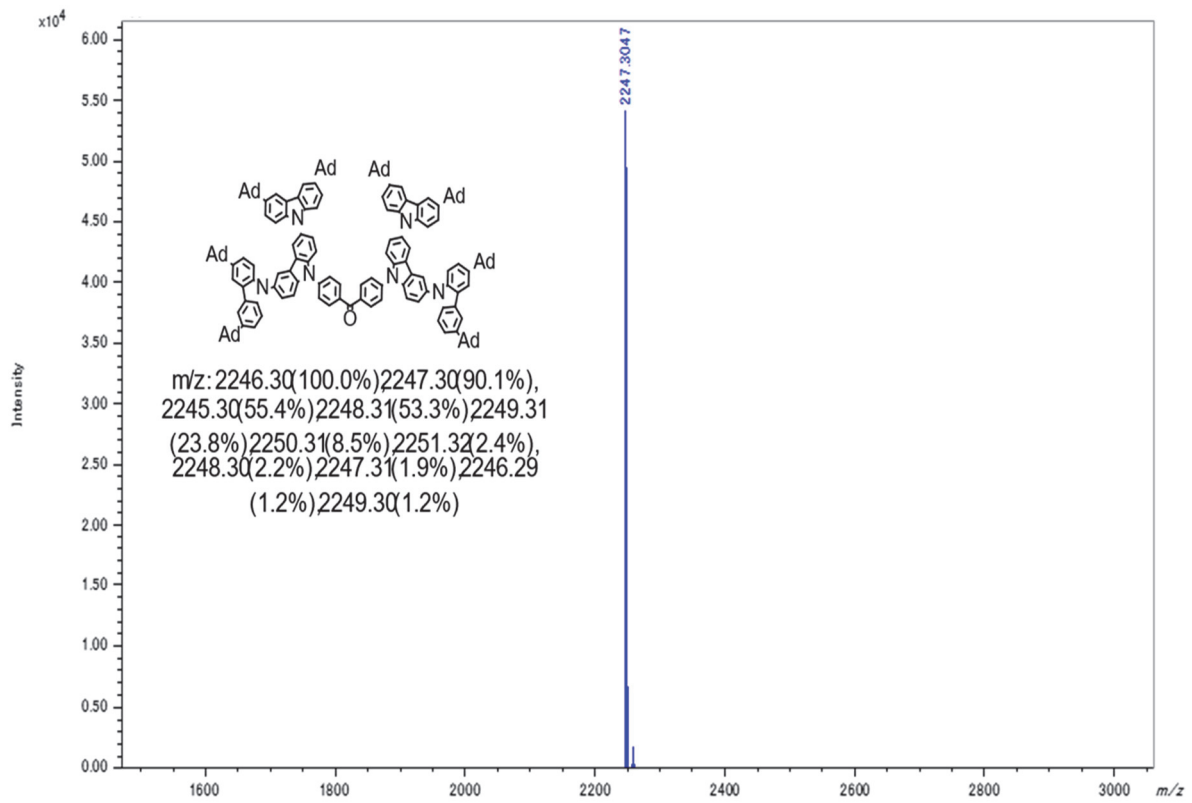


Figure S26. MALDI TOF-MS spectrum of AdCz.



**Figure S27 MALDI TOF-MS spectrum of AdG2on.**



**Figure S28 MALDI TOF-MS spectrum of AdG2B.**

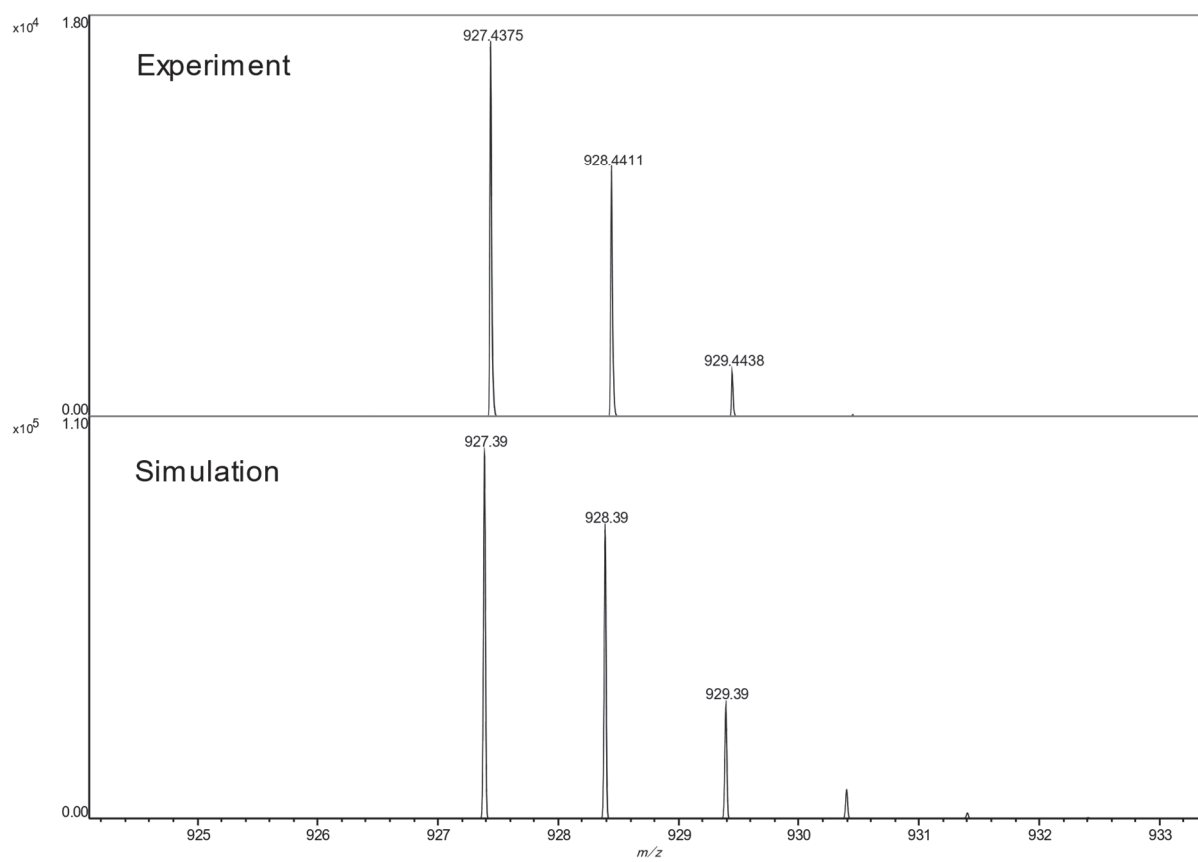
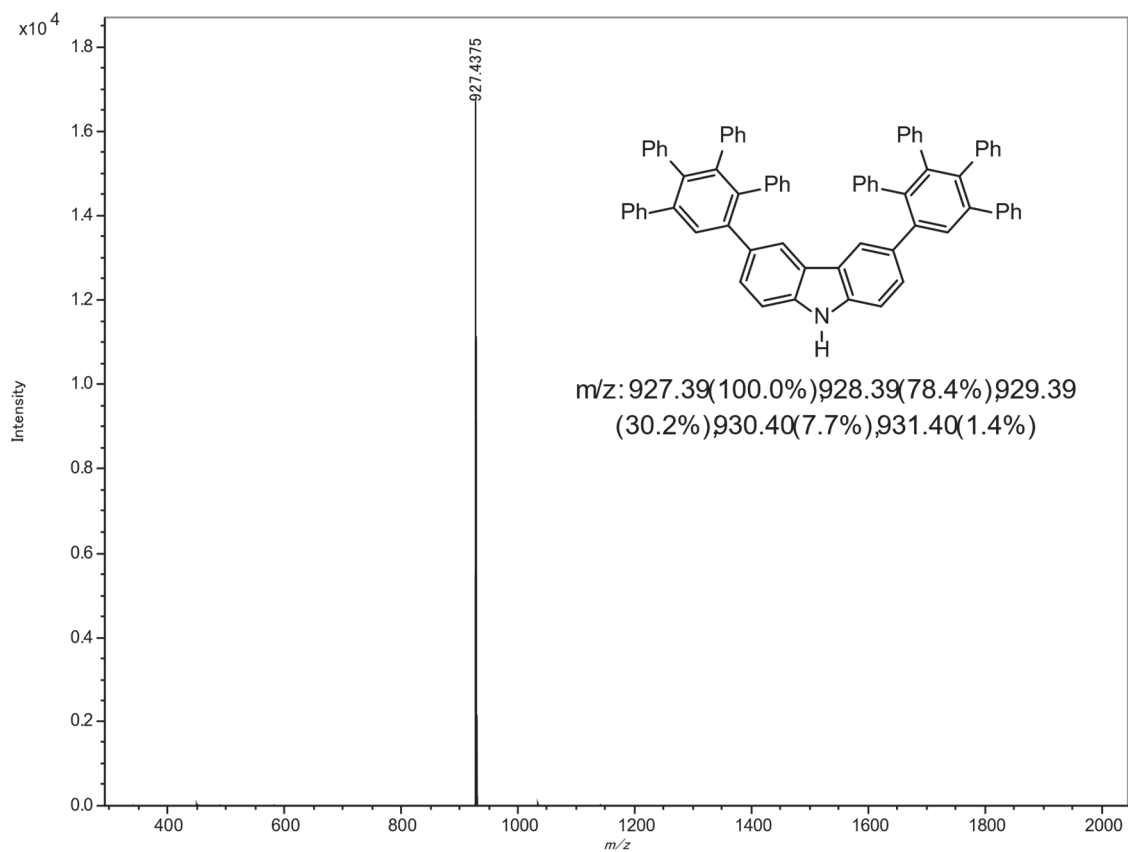


Figure S29 MALDI TOF-MS spectrum of TPPhCz.

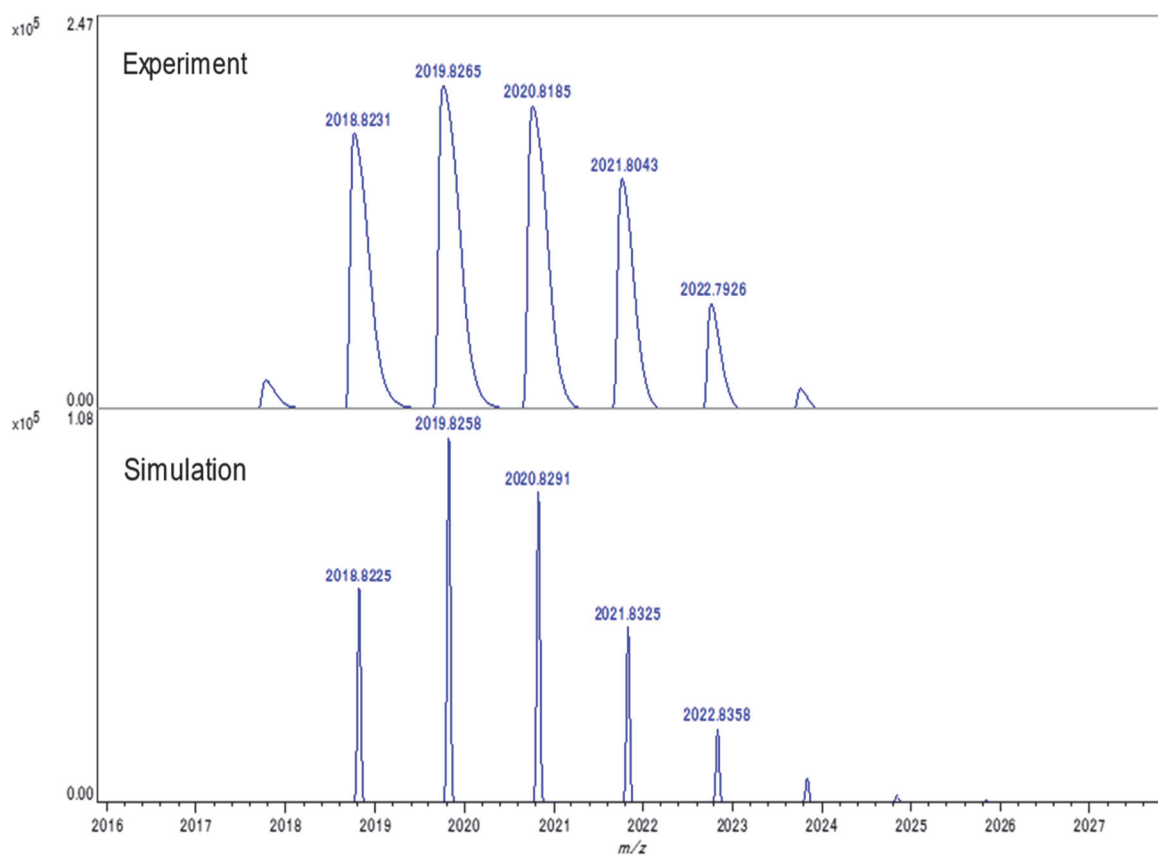
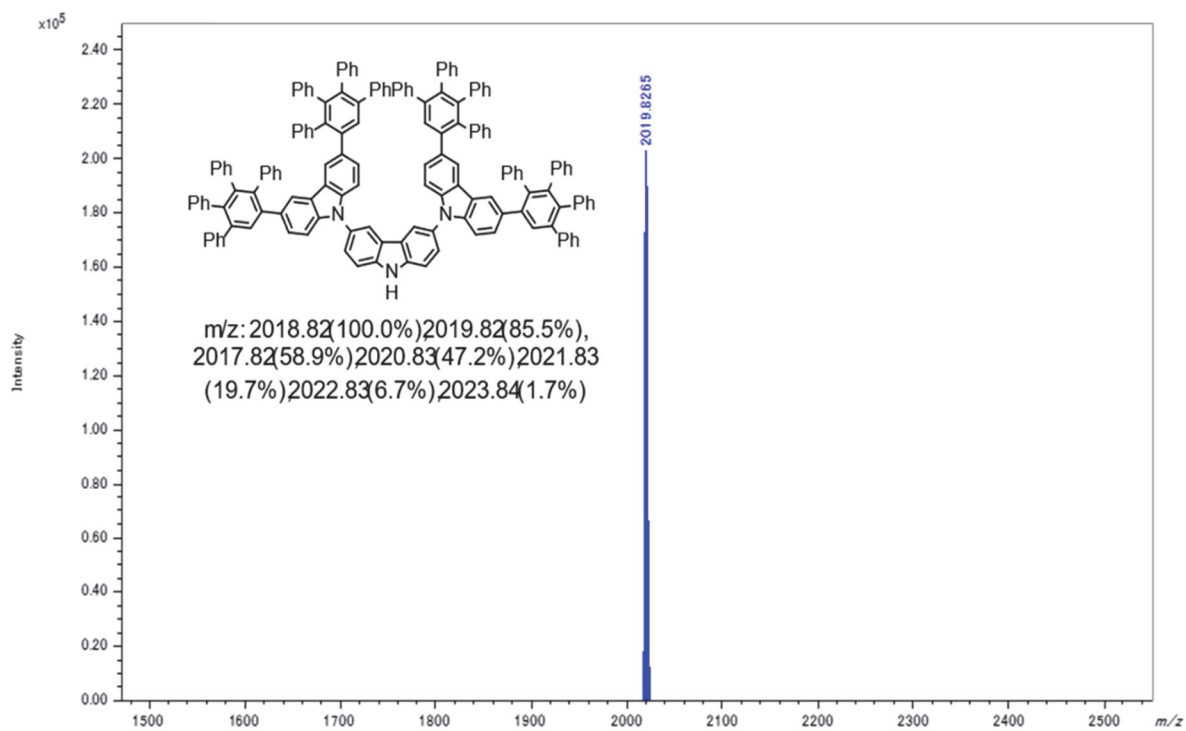


Figure S30 MALDI TOF-MS spectrum of TPPhG2on.



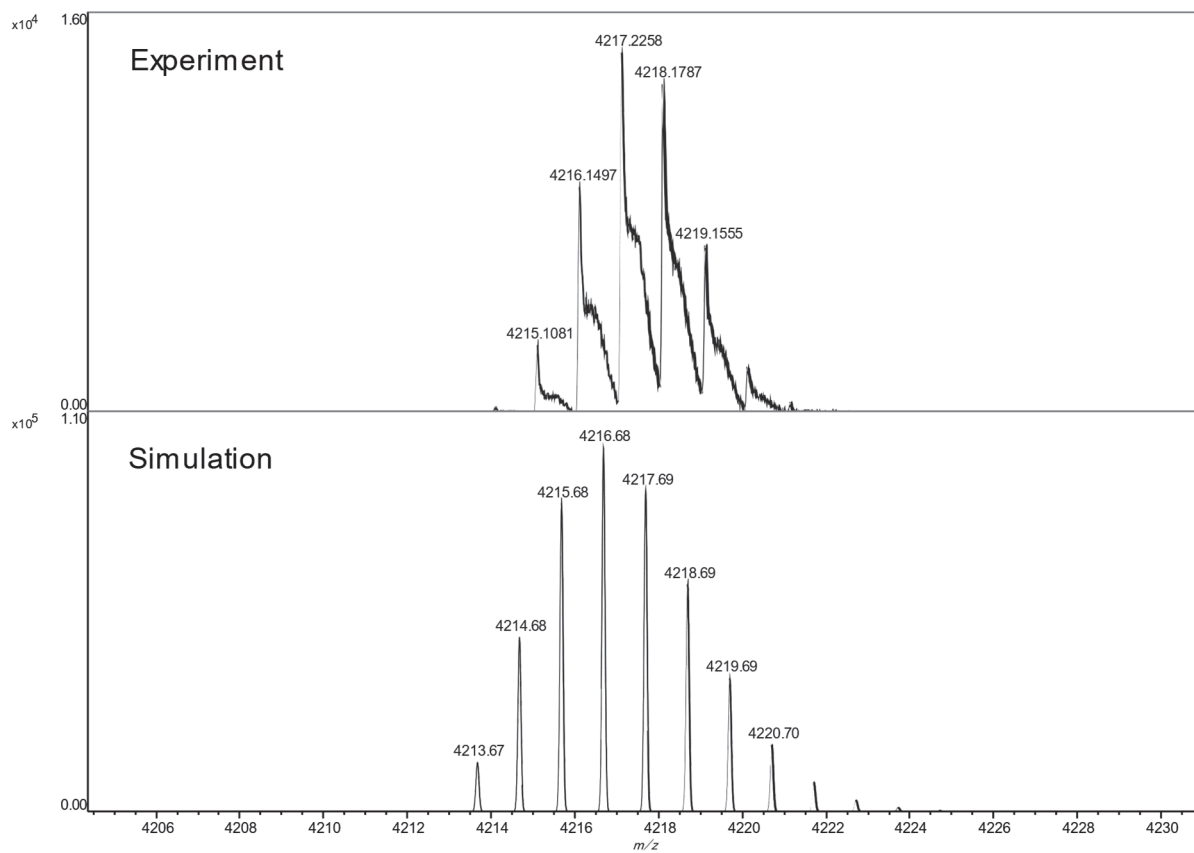
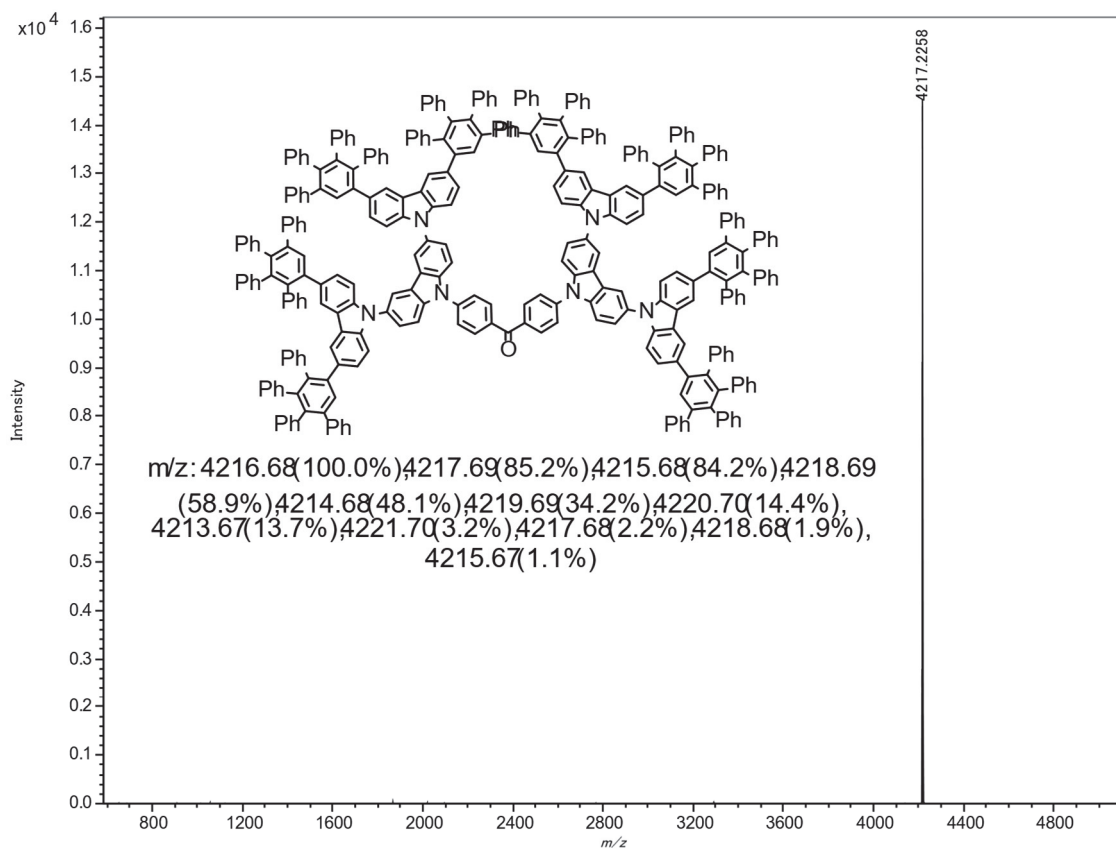


Figure S31 MALDI TOF-MS spectrum of TPPhG2B.