Electronic supplementary information for

Fluorescent Molecular Glass Based on Hexadehydrotribenzo[12]annulene

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1. TG chart of C8[12]DBA

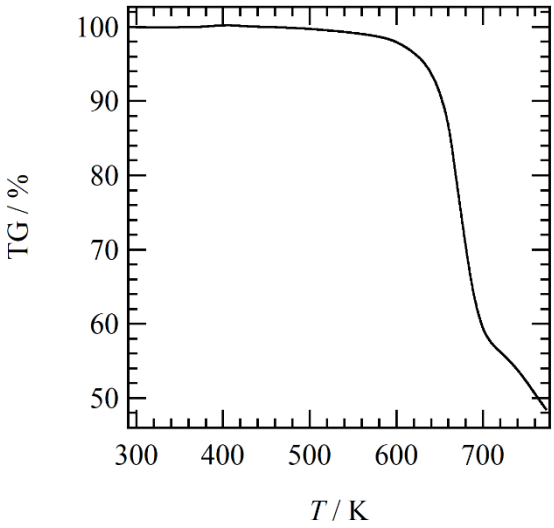


Figure S1 TG curve of **C8[12]DBA**.

2. ORTEP drawings of C1[12]DBA

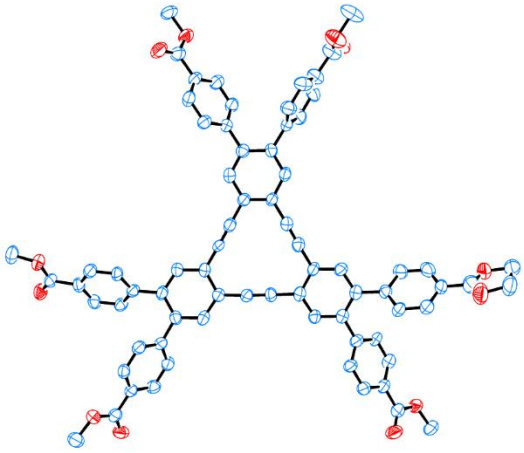


Figure S2 ORTEP drawing of **C1[12]DBA**. Displacement ellipsoids are drawn at the 50% probability level. One of six methyl ester groups had a disordered structure. Hydrogen atoms and solvent toluene molecule are omitted for clarity.

3. HOMO and LUMO of C1[12]DBA

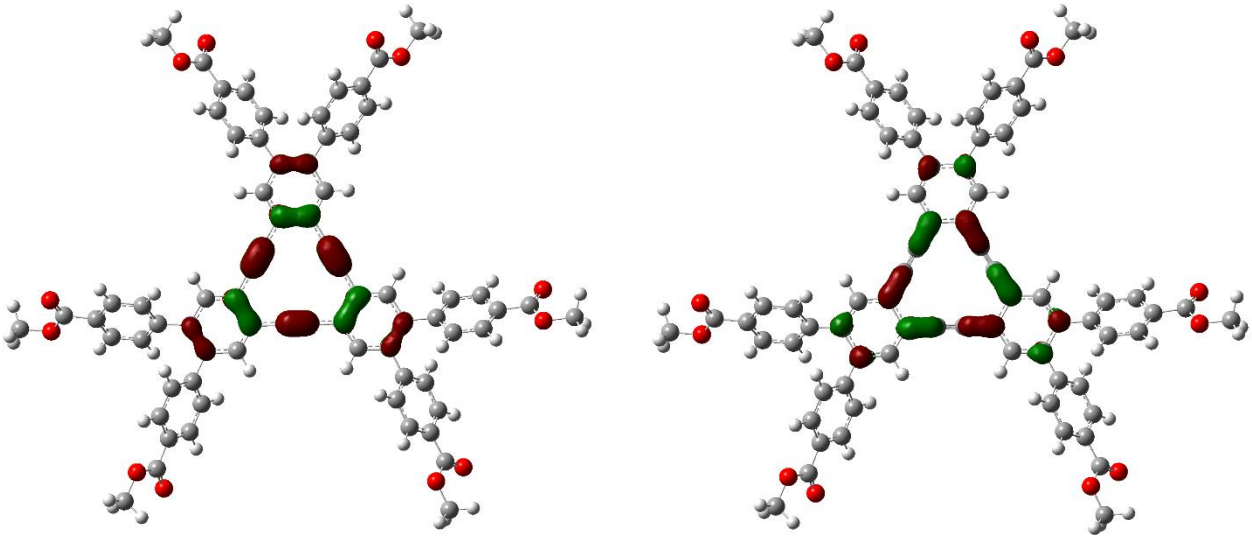


Figure S3 HOMO (left) and LUMO (right) of the optimized structure of **C1[12]DBA**

4. UV-Vis and fluorescent spectra of C1[12]DBA in solution and in the solid state

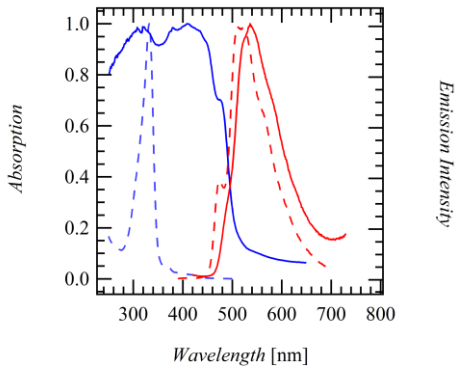


Figure S4 UV-Vis (blue) and fluorescent (red) spectra of **C1[12]DBA** in solution ($CHCl_3$, dotted line) and in the solid state (solid line).

5. Experimental section

General methods. Commercially available reagents and solvents were used as received. **[12]DBACA** was prepared by as described in the literature.[S1] ^1H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded on a Bruker Avance III 400 NMR spectrometer. Chemical shifts (δ) are expressed in ppm with reference to tetramethylsilane (^1H 0.00 ppm) or residual nondeuterated solvent ($CDCl_3$; ^{13}C 77.0 ppm) as an internal standard. Mass spectra were recorded on a JMS-700 spectrometer at the NMR and MS Laboratory, Graduate School of Agriculture, Tohoku University. Elemental analyses were performed on a Microcoder JM10 at the

Elementary Analysis Laboratory, Institute of Multidisciplinary Research for Advanced Materials, Tohoku University. IR spectra were measured on a Thermo Scientific NICOLET 6700 FT-IR spectrometer.

Preparation of C8[12]DBA.

A mixture of **[12]DBACA** (101 mg, 98.7 μmol), 1-octanol (10 mL) and conc. H_2SO_4 (a few drops) was stirred at 150 °C for 18 h. After cooling to rt, the reaction mixture was diluted with $CHCl_3$ and water. The aqueous phase was separated and extracted with $CHCl_3$. The combined organic layer was washed with water and brine, and then dried over $MgSO_4$. After evaporation of solvent under reduced pressure, the crude product was purified by silica gel column chromatography and GPC to give **C8[12]DBA** (124 mg, 74%) as a yellow waxy solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (d, J = 8.4 Hz, 12H), 7.47 (s, 6H), 7.18 (d, J = 8.4 Hz, 12H), 4.29 (t, J = 6.8 Hz, 12H), 1.75 (quint., J = 7.1 Hz, 12H), 1.28–1.45 (m, 60H), 0.88 (t, J = 7.0 Hz, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 143.9, 140.1, 134.1, 129.5, 129.4, 126.3, 93.2, 65.3, 31.8, 29.21, 29.15, 28.6, 26.0, 22.6, 14.1. (one aromatic carbon signal overlapped) IR 2955, 2926, 2855, 1720, 1608, 1489, 1467, 1405, 1381, 1310, 1273, 1179, 1115, 1103, 1017, 952, 904, 857, 777, 711 cm^{-1}. HRMS (FAB) calcd for $C_{114}H_{133}O_{12}$: 1693.9797 [$(M+H)^+$]; found: 1693.9800. Elem. Anal.: Calc. for $C_{114}H_{132}O_{12}$: C, 80.82 %; H, 7.85 %; Found: C, 80.60 %; H, 7.92 %.

Physical measurement. Thermogravimetric (TG) analysis was performed on a Rigaku Thermoplus EVO 2 at a scan rate of 10 K/min under a nitrogen atmosphere. Differential scanning calorimetry (DSC) analysis was conducted using a Mettler Toledo DSC-1 at a scan rate of 10 K/min. Temperature-dependent dielectric constants of the compounds were measured using a two-probe AC impedance method at a frequency range of 1 kHz to 1 MHz (Hewlett-Packard, HP4194A) with a liquid crystal cell in a Linkam LTS350 temperature-control system. The melt of **C8[12]DBA** was fabricated on indium tin oxide(ITO) glass (SZ-A311P6N), which was sandwiched by a corresponding ITO glass to form a dielectric measurement cell with an average electrode gap of 56 μm, and electrode area of 0.9 cm^2.

X-ray structural analysis. Crystallographic data for single crystals were collected using a diffractometer equipped with a rotating anode fitted with a multilayer confocal optic using Cu-Kα (λ = 1.54187 Å) radiation. Structure refinements were carried out using the full-matrix least-squares method on F^2. Calculations were performed using the Crystal Structure and SHELEX software packages.[S2] Parameters were refined using anisotropic temperature factors, except for the hydrogen atom.

Crystal data of C8[12]DBA·(toluene): A single-crystalline sample was obtained by recrystallization from toluene. $C_{79}H_{56}O_{12}$, M = 1197.30, $P2_1/n$ (#14), a = 24.3648(9) Å, b = 9.5585(4) Å, c = 25.8540(10) Å, β = 94.315(7) °, V = 6004.1(4) Å^3, Z= 4, Dc= 1.324 g cm^{-3}. Independent reflections 10960 (all), T = 100 K, μ= 7.19 cm^{-1}, R = 9.73%. CCDC 2069905.

DFT caluculations. DFT calculations were performed with the Gaussian 16[S3] program package. The optimized molecular structure of **C1[12]DBA** was obtained by DFT calculations with the B3LYP/6-31G (d,p) basis set. The stationary point was assessed by a vibration frequency analysis.

6. ^{1}H and ^{13}C NMR spectra of C8[12]DBA

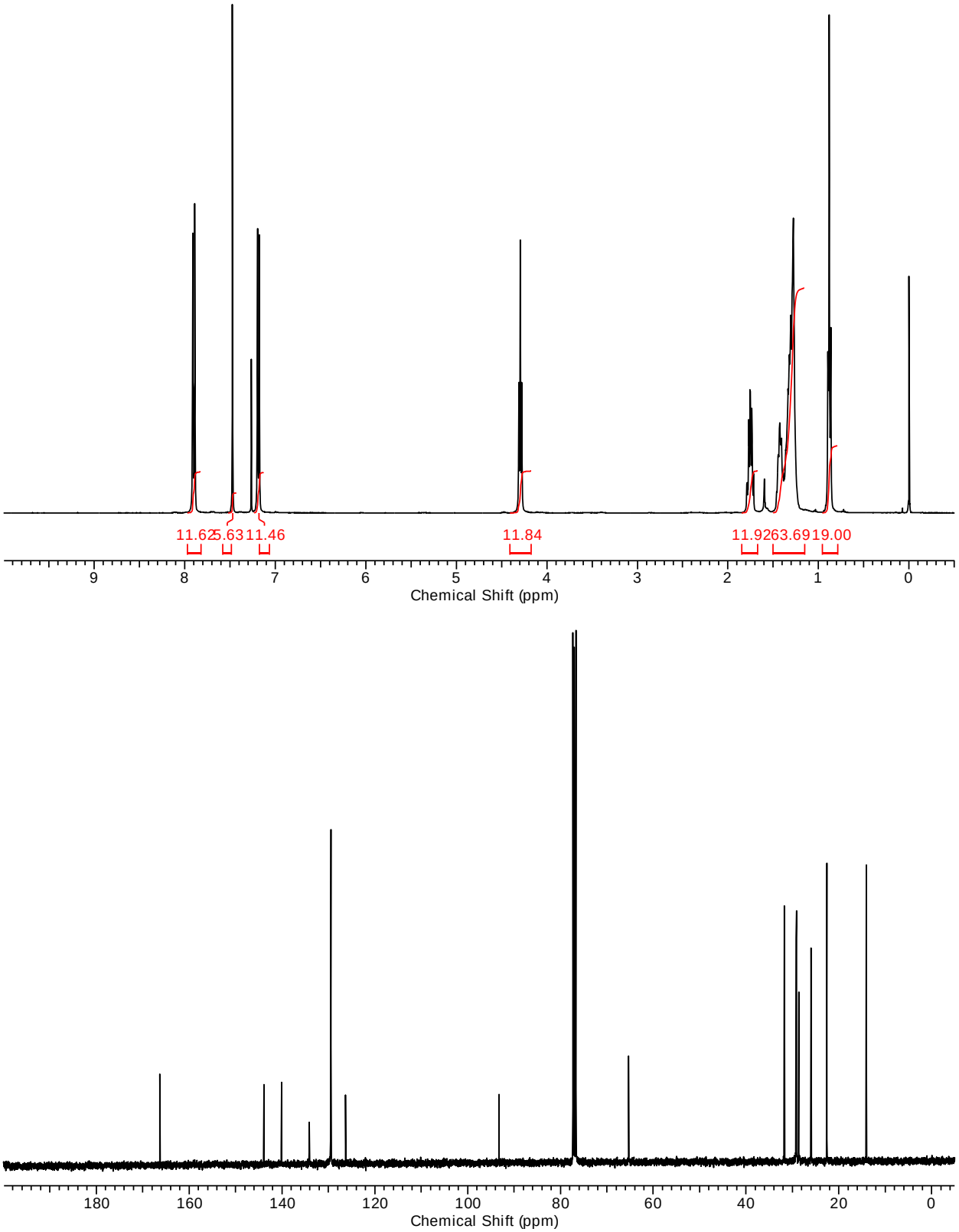
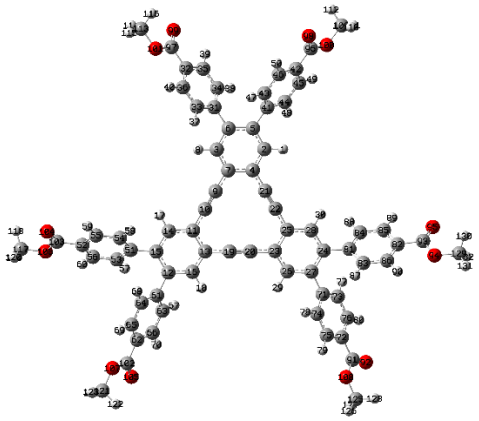


Figure S5 ^{1}H (top) and ^{13}C (bottom) NMR spectra of **C8[12]DBA** in $CDCl_3$.

7. Cartesian coordinates for optimized structure of C1[12]DBA



E(RB3LYP) = -3675.31177702 a.u.

Number of imaginary frequencies: 0

Atom Number	Element	X	Y	Z
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2	C	2.270187	3.603688	-0.021074
3	C	-0.421340	4.224541	0.016601
4	C	1.340926	2.554406	-0.029560
5	C	1.892327	4.952206	0.009800
6	C	0.509578	5.271265	0.014020
7	C	-0.046160	2.874248	-0.001556
8	H	-1.479191	4.463225	-0.001260
9	C	-1.031341	1.849998	-0.001966
10	C	-1.859676	0.959705	-0.000561
11	C	-2.812389	-0.094686	0.001236
12	C	-4.750779	-2.172590	0.007699
13	C	-2.396865	-1.456305	-0.018984
14	C	-4.185704	0.186021	0.011387
15	C	-5.164925	-0.815405	0.005692
16	C	-3.379146	-2.456206	-0.013226
17	H	-4.497190	1.224726	-0.010924
18	H	-3.056785	-3.491612	0.009058
19	C	-1.017430	-1.797893	-0.033306
20	C	0.167568	-2.070425	-0.048004
21	C	1.777574	1.202198	-0.052825
22	C	2.132859	0.039387	-0.071530
23	C	1.557183	-2.367680	-0.068240
24	C	4.325491	-3.004648	-0.117842
25	C	2.527365	-1.325784	-0.088863
26	C	2.001525	-3.696980	-0.082352
27	C	3.358530	-4.043037	-0.114387
28	C	3.884603	-1.675245	-0.112917

Atom Number	Element	X	Y	Z
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68	H	-6.813344	-2.562460	1.761566
69	H	-8.301936	-4.528716	1.924787
70	H	-6.297821	-6.347504	-1.398046
71	C	3.703041	-5.490201	-0.193781
72	C	4.246083	-8.247700	-0.388181
73	C	4.567549	-5.983818	-1.186596
74	C	3.114444	-6.405334	0.695642
75	C	3.383328	-7.768027	0.605236
76	C	4.833276	-7.343832	-1.283859
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78	H	2.452527	-6.039368	1.474866
79	H	2.929929	-8.462412	1.302900
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43	C	2.969629	6.971686	1.076487
44	C	4.062874	5.915737	-0.800319
45	C	5.109832	6.828509	-0.711008
46	C	4.015861	7.880397	1.172747
47	H	2.145220	7.024511	1.779373
48	H	4.076513	5.156892	-1.576919
49	H	5.939343	6.780007	-1.406687
50	H	4.021372	8.647458	1.939399
51	C	-6.591177	-0.388418	-0.050441
52	C	-9.253999	0.518648	-0.201496
53	C	-7.468030	-0.891951	-1.026446
54	C	-7.073245	0.581905	0.845304
55	C	-8.388526	1.027138	0.774550
56	C	-8.782120	-0.443798	-1.104861
57	H	-7.111248	-1.631693	-1.735116
58	H	-6.412168	0.974715	1.612012
59	H	-8.767496	1.768300	1.469824
60	H	-9.446232	-0.833272	-1.867521
61	C	-5.694484	-3.322942	0.081255
62	C	-7.392964	-5.562471	0.268094
63	C	-5.555213	-4.407933	-0.801896
95	O	10.824126	-3.197660	-0.719257
96	C	6.185160	8.821167	0.429780
97	C	-1.654313	10.638386	-0.285864
98	O	6.210141	9.689212	1.280398
99	O	-1.296603	11.447952	-1.119104
100	O	7.163034	8.662596	-0.492494
101	O	-2.600875	10.905055	0.644193
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66	C	-6.395388	-5.512235	-0.713115	132	H	12.290284	-5.200606	0.168578

8. Reference

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