Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Excited-State Localization and Energy Transfer in Pyrene Core Dendrimers with Fluorene/ Carbazole as Dendrons, and Acetylene as Linkages

Linyin Yan, Yan Wan, Andong Xia*

The State Key Laboratory of Molecular Reaction Dynamics, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, P. R. China

Beijing National Laboratory for Molecular Sciences (BNLMS), Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, P. R. China

*ShengHien Lin**

Department of Applied Chemistry, National Chiao Tung University, Hsinchu, Taiwan 30010, China

Ran Huang

School of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, Shanghai 200240, China

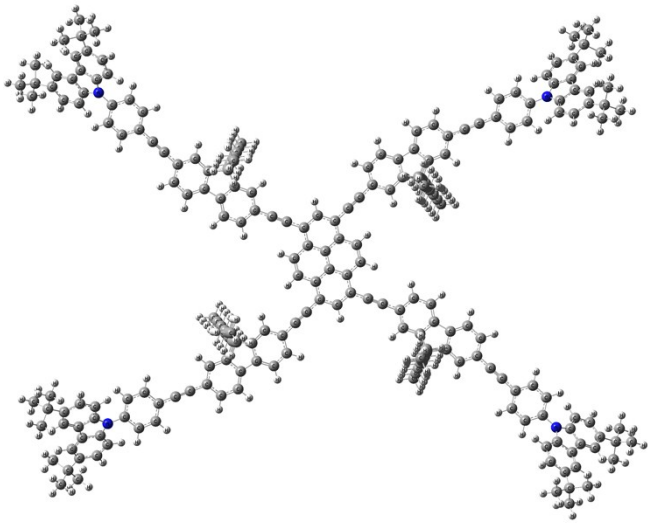


Figure S1 Optimized Molecular Structures of T1

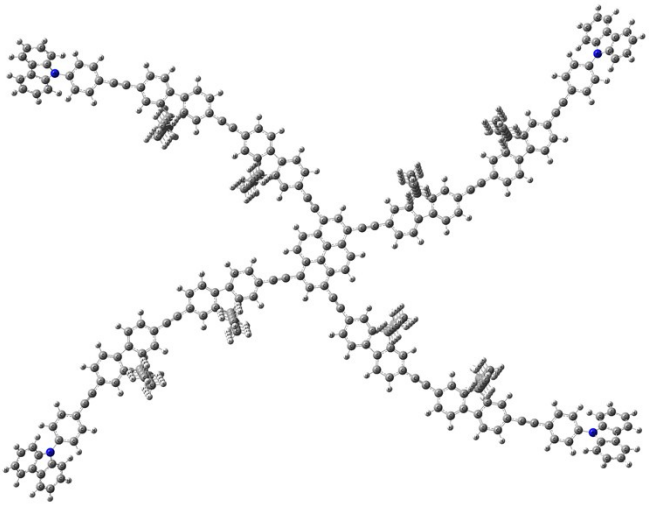


Figure S2 Optimized Molecular Structures of T2

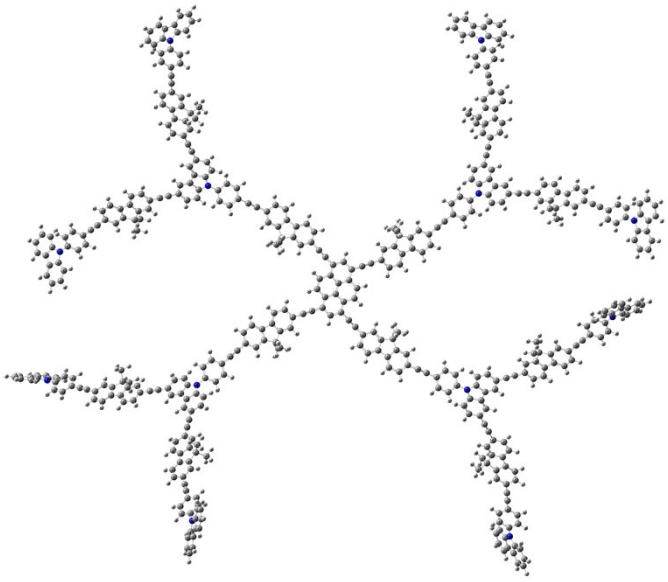


Figure S3 Optimized Molecular Structures of T3

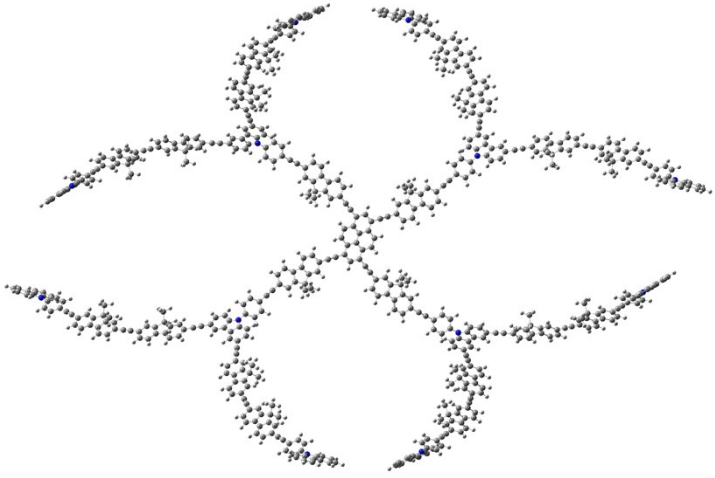


Figure S4 Optimized Molecular Structures of T4

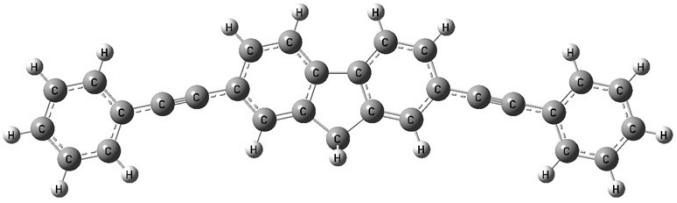


Figure S5 Optimized Molecular Structures of the **Chromophore B**

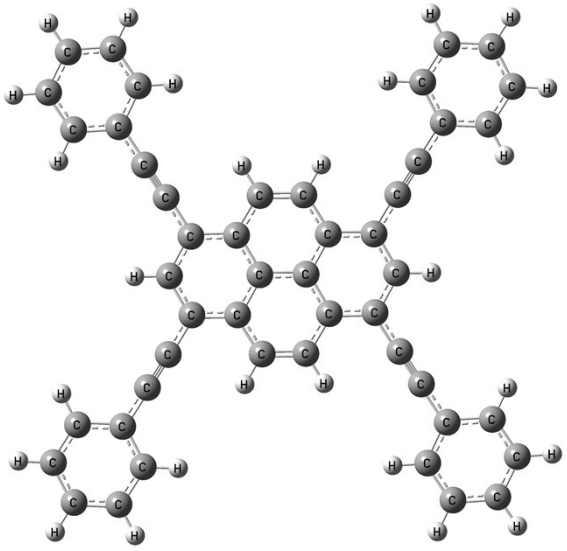


Figure S6 Optimized Molecular Structures of the **Chromophore C**

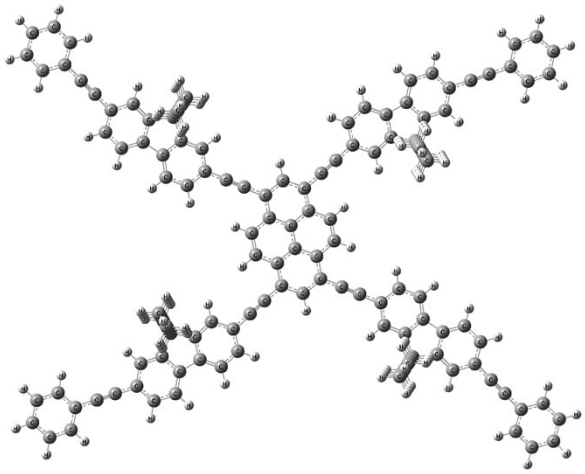


Figure S7 Optimized Molecular Structures of the Molecule Model 1 **(M1)**

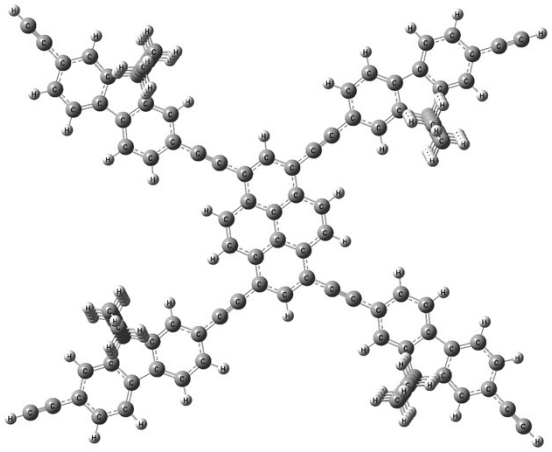


Figure S8 Optimized Molecular Structures of the Molecule Model 2 **(M2)**

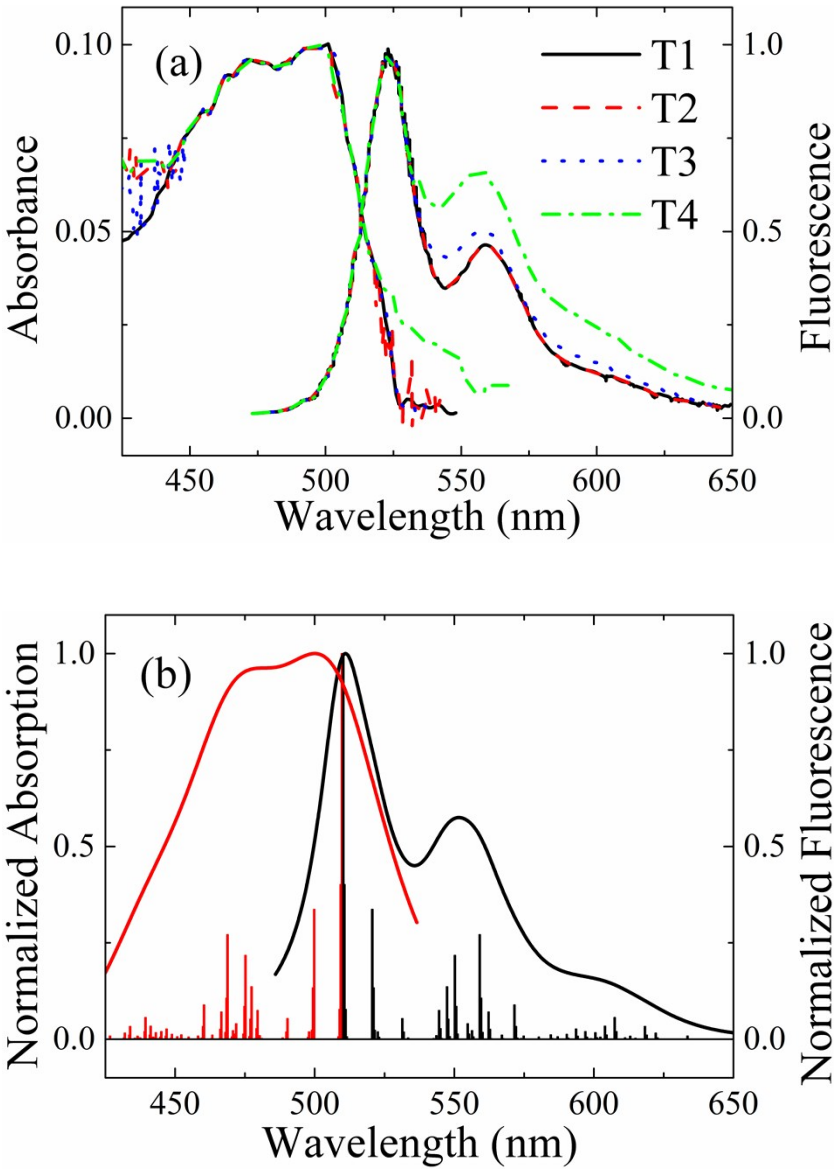


Figure S9. Normalized absorption and fluorescence spectra of dendrimers obtained by experimental detection in toluene (1.0×10^{-5} M) (a) and theoretical calculation (b)[8]. To better describe the spectra, Lorentzian line shapes with different FWHMs have been used of absorption and emission bands. For the absorption band, FWHM = 1000 cm^{-1}, and for the emission one FWHM = 500 cm^{-1}.

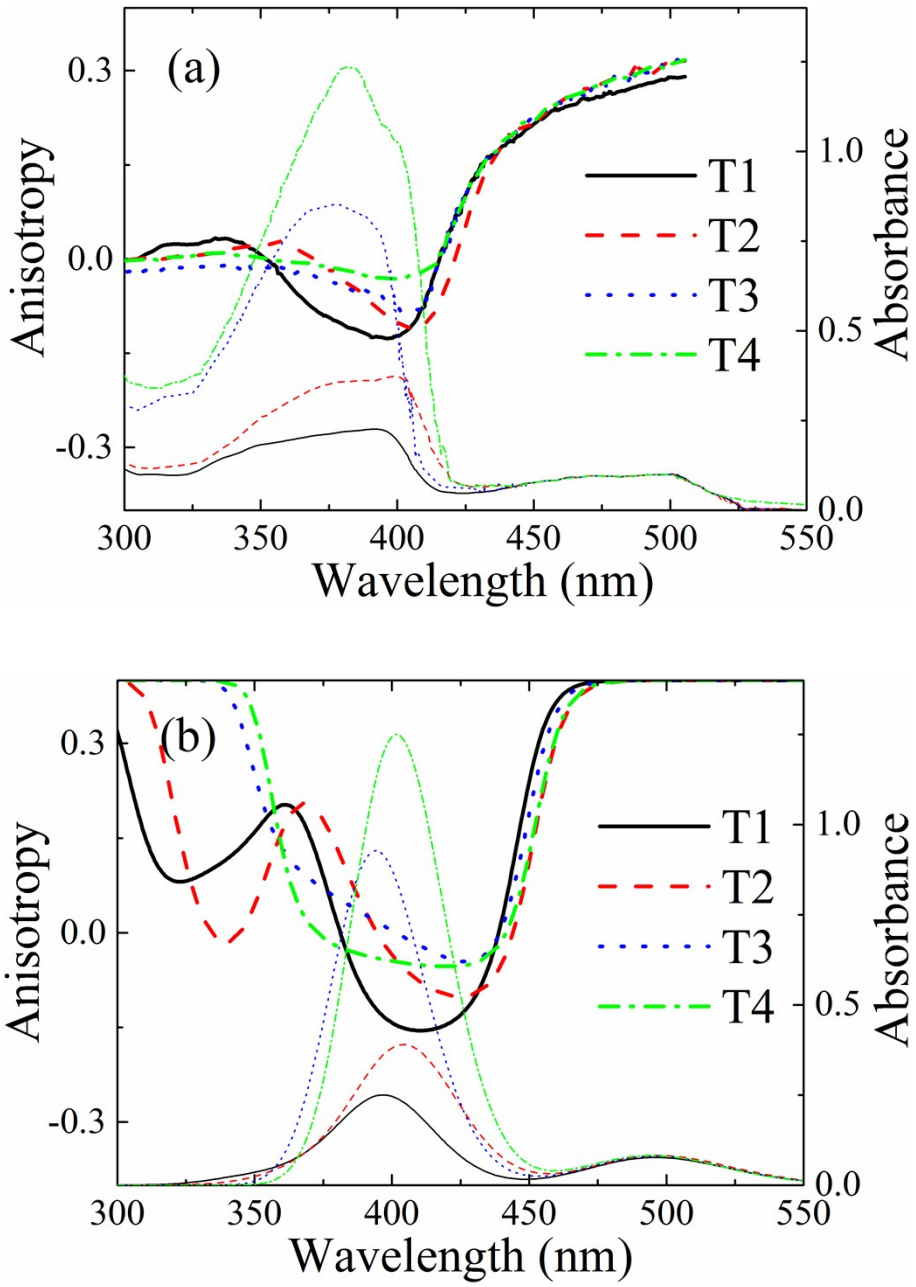


Figure S10. Fluorescence excitation anisotropy spectra and absorption spectra of T1-T4, obtained by experimental detection (a)[8] , and theoretical calculation (b).

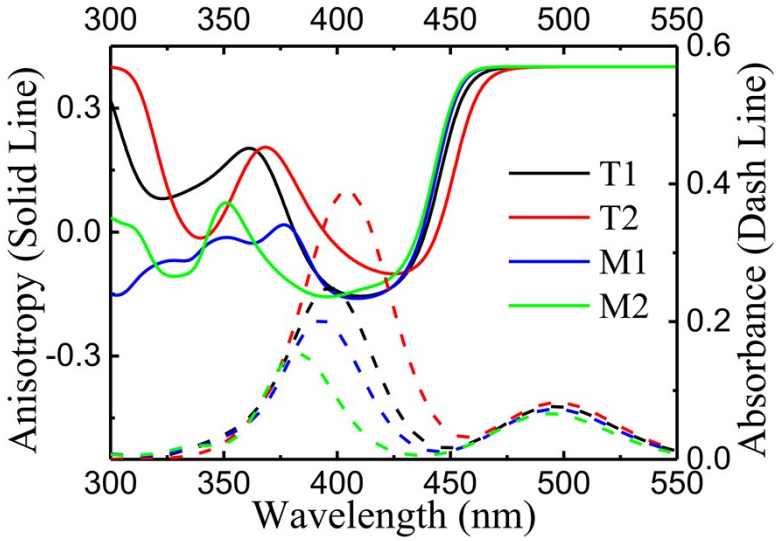


Figure S11. Fluorescence excitation anisotropy spectra and absorption spectra of T1 and M1 M2, obtained by theoretical calculation.

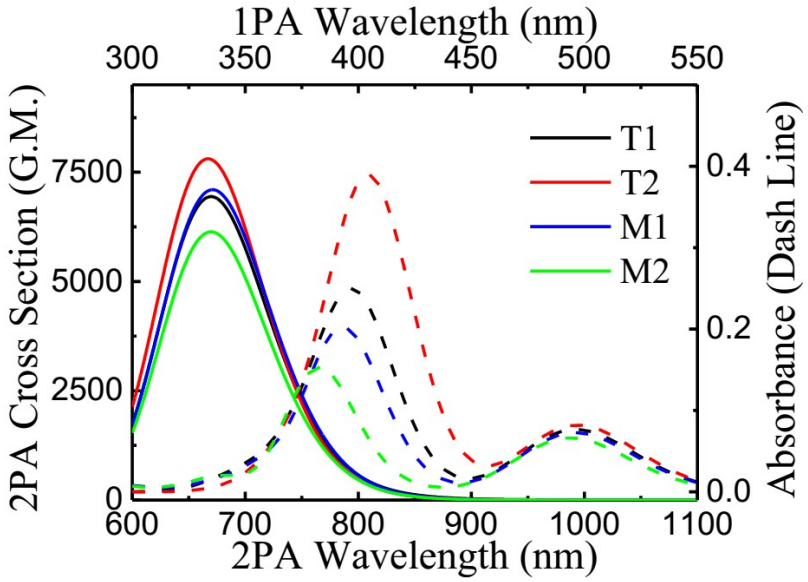
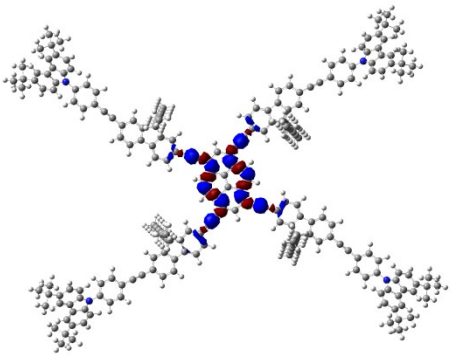
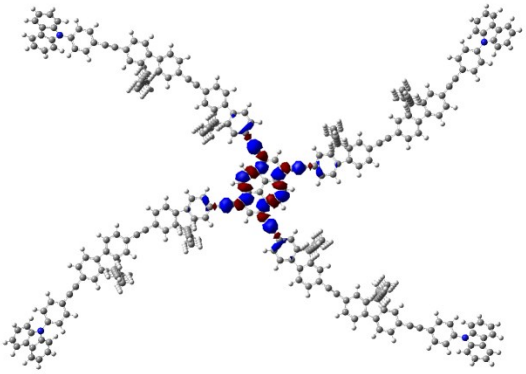
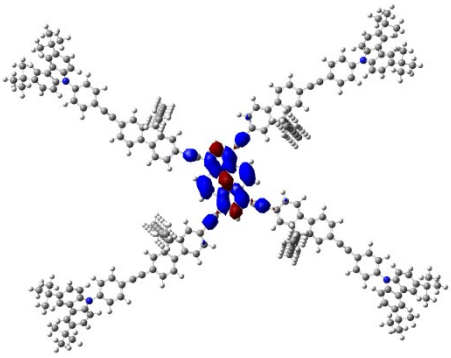
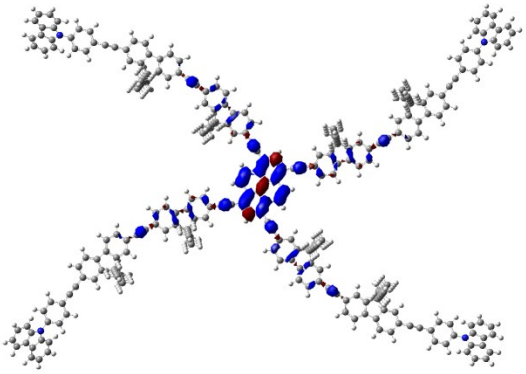
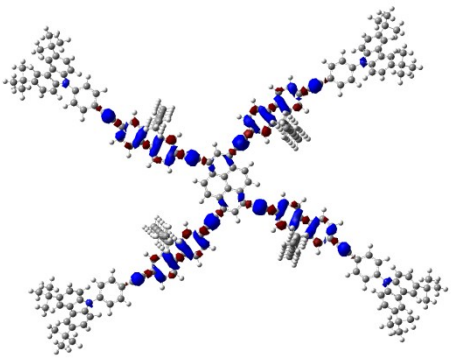
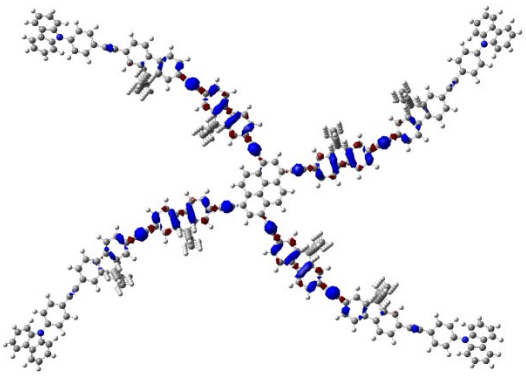
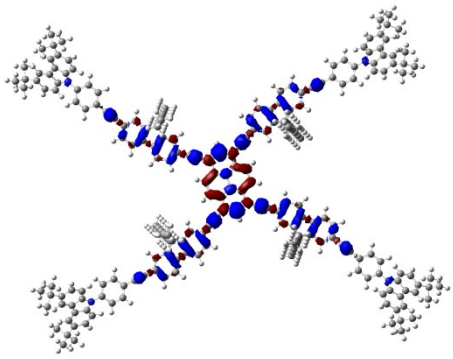
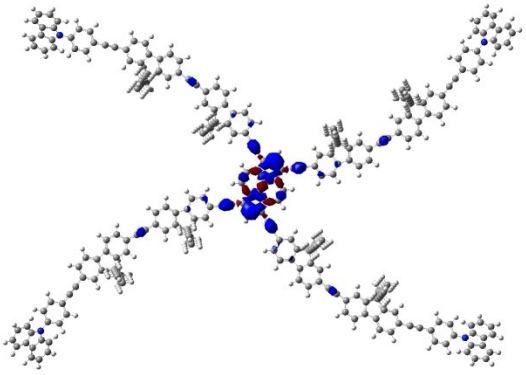
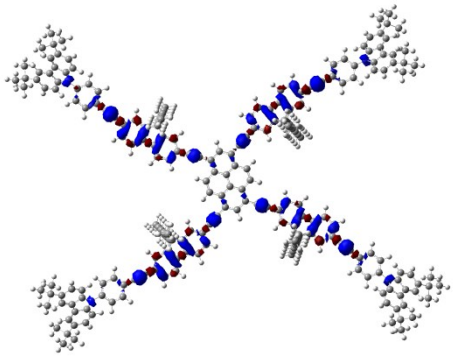
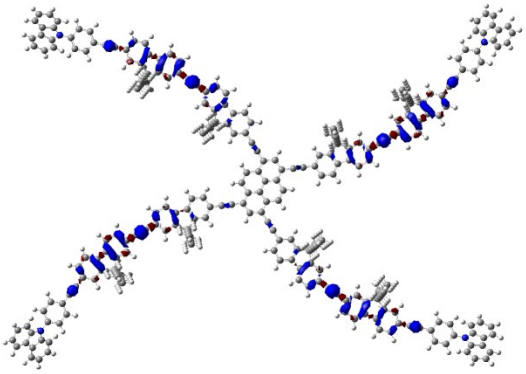
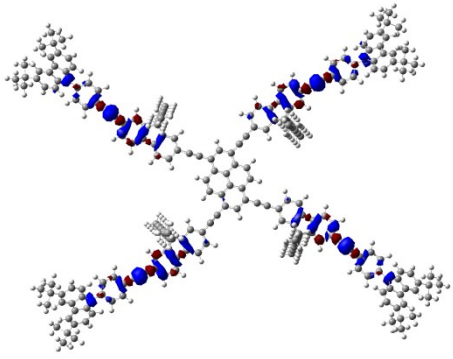
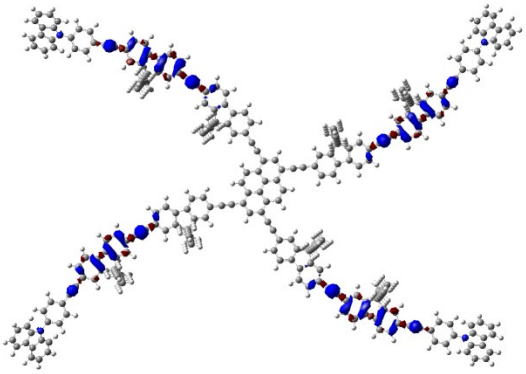


Figure S12. Simulated two-photon absorption (2PA, solid lines) and one-photon absorption (1PA, dash lines) spectra of T1 and M1 M2.

Table S1. Calculated Excited States Charge Difference density (CDD) of T1 and T2.[a]

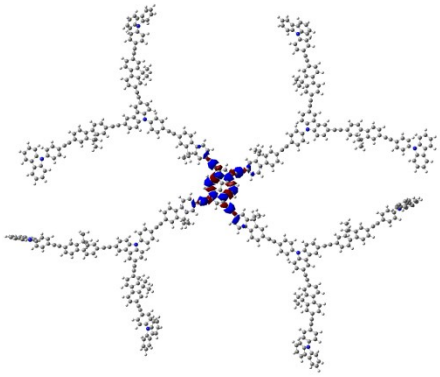
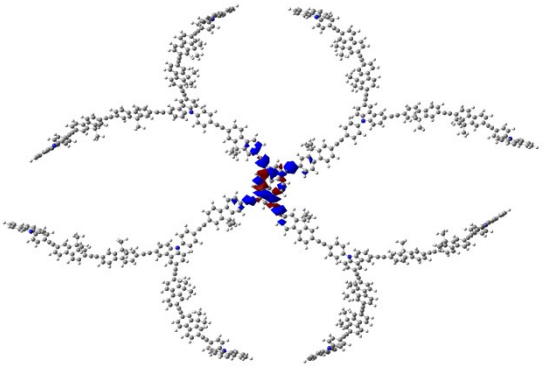
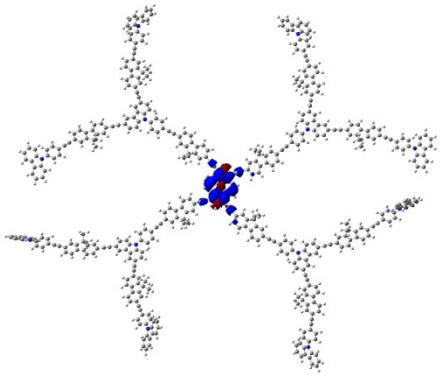
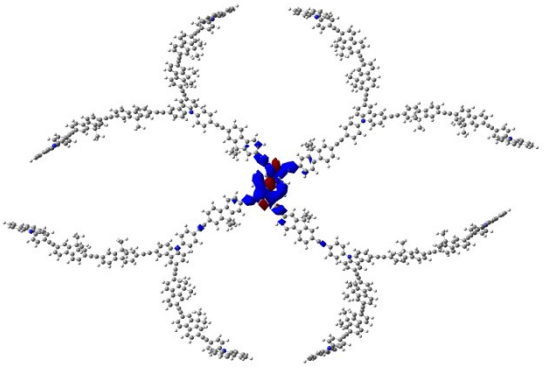
Transition	T1	T2
S_0-S_1		
	2.50 eV 496 nm f=1.9435 **494nm**	2.49eV 497 nm f=2.0796 **496nm**
S_0-S_2		
	3.05 eV 406 nm f=1.3693 **392nm**	3.03eV 410 nm f=5.8950 **398nm**
S_0-S_3		

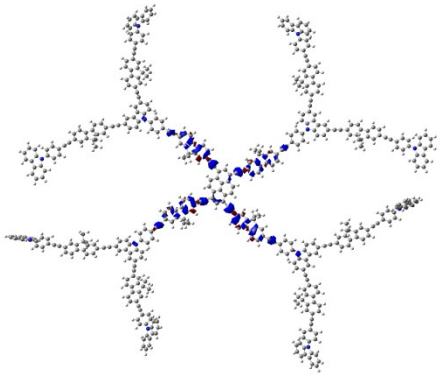
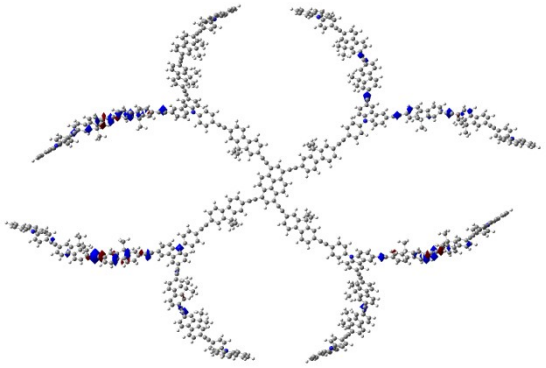
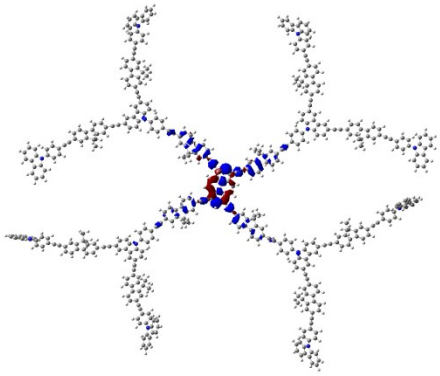
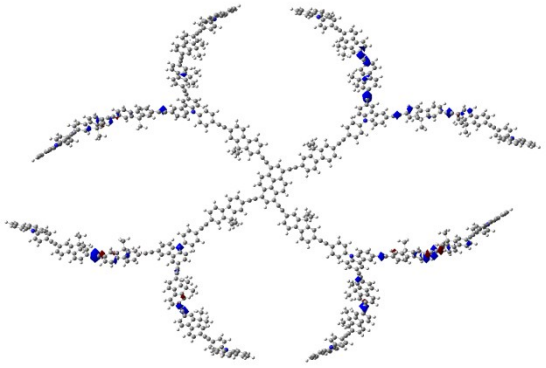
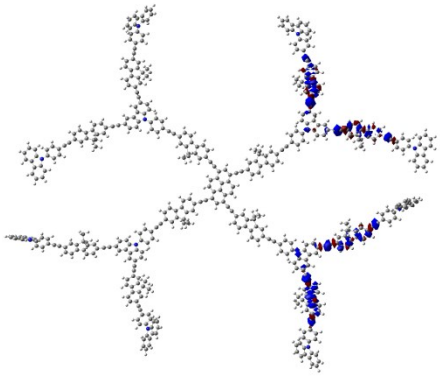
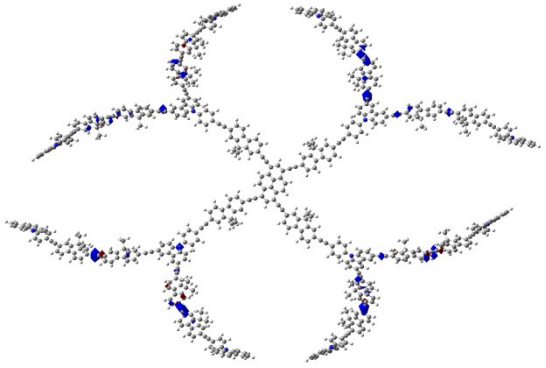
	3.12 eV 398 nm f=0.0006	3.05 eV 407 nm f=0.0003
S_0-S_4		
	3.13 eV 396 nm f=4.9114 **392nm**	3.08 eV 402 nm f=2.6836 **398nm**
S_0-S_5		
	3.29 eV 377 nm f=0.0045	3.1655 eV 391.67 nm f=0.0078
S_0-S_6		
	3.35 eV 370 nm f=1.2177	3.1736eV 390.68nm f=2.1371 **398nm**

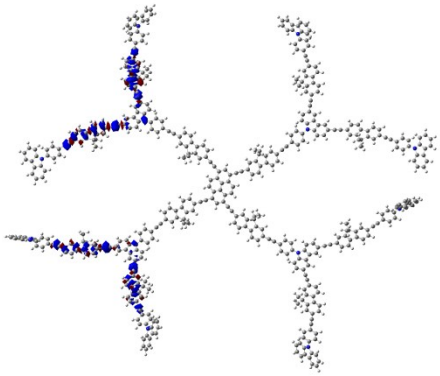
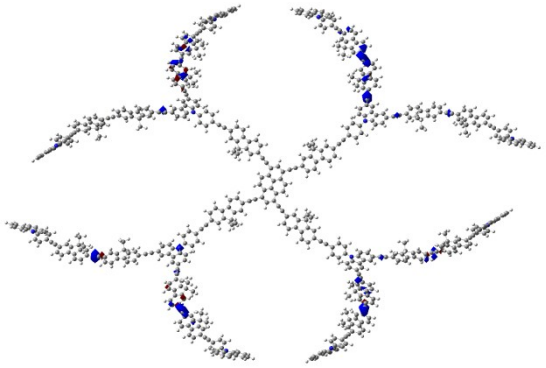
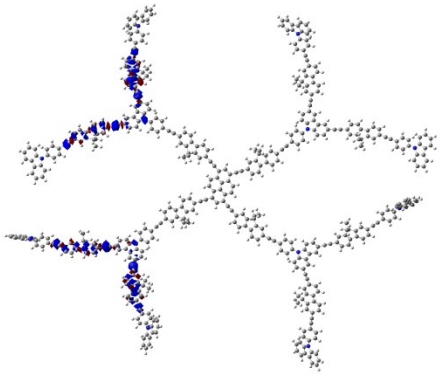
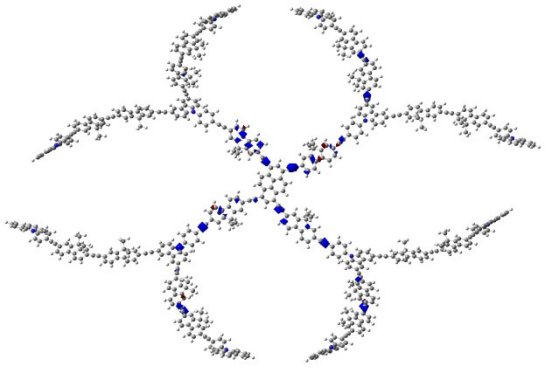
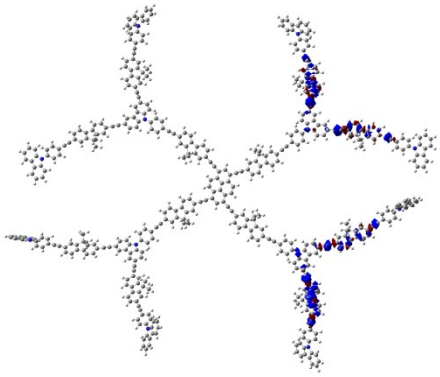
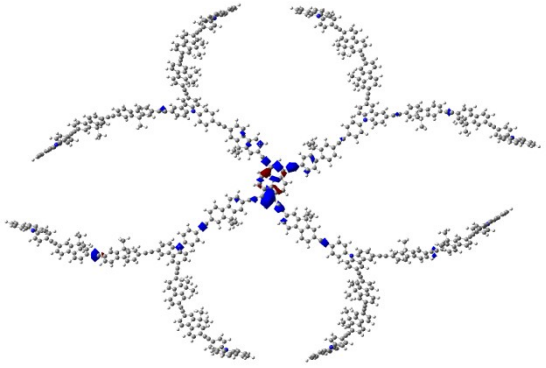
[a] The negative density (blue) represents the hole, and the positive density (red) represent the electron. Calculated excitation energy and oscillator strength (f) are listed in the table. The

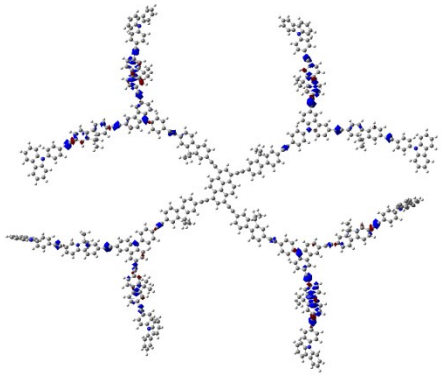
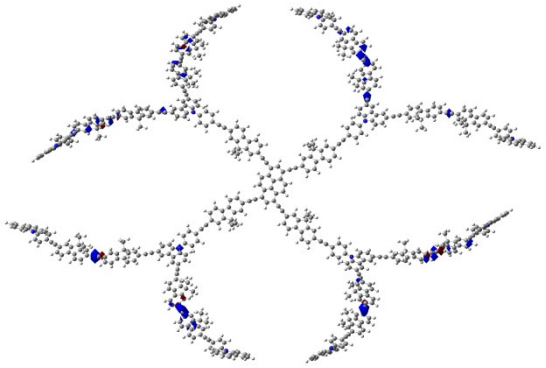
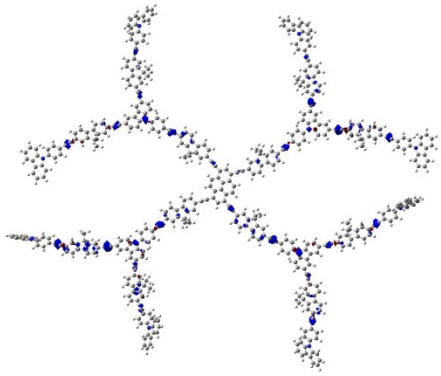
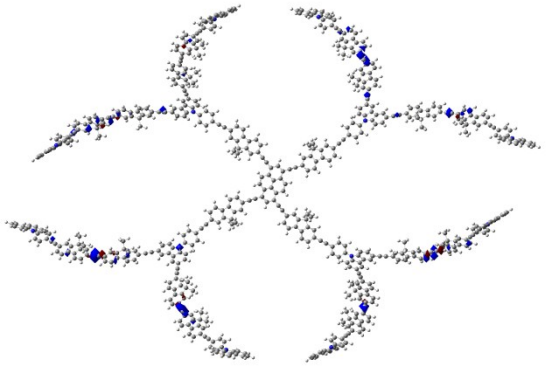
detected absorption maximums are also listed in the corresponding table in bold type. The density data shown in this table were obtained by using ZINDO method.

Table S2. Calculated Excited States Charge Difference density (CDD) of T3 and T4.[a]

Transition	T3	T4
S_0-S_1		
	2.50 eV 495 nm f=2.0378 **494nm**	2.51 eV 494 nm f=2.0805 **494nm**
S_0-S_2		
	3.05 eV 407 nm f=2.5162	3.05 eV 407 nm f=3.3284

S_0-S_3		
	3.10 eV 400 nm f=0.0163	3.08 eV 403 nm f=0.0076
S_0-S_4		
	3.12 eV 398 nm f=6.7340 **377nm**	3.08 eV 403 nm f=3.0270
S_0-S_5		
	3.15 eV 393 nm f=1.5513	3.08 eV 402 nm f=0.0009

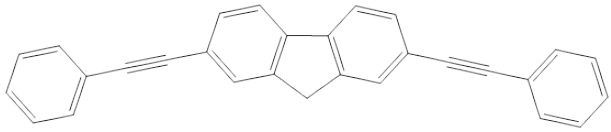
S_0-S_6		
	3.16 eV 393 nm f=3.2680	3.09 eV 402 nm f=16.5376 **383nm**
S_0-S_7		
	3.16 eV 392 nm f=1.8557	3.09 eV 402 nm f=0.0236
S_0-S_8		
	3.17 eV 392 nm f=6.1214 **377nm**	3.10 eV 400 nm f=7.3510 **383nm**

S_0-S_9		
	3.21 eV 385 nm f=2.7466	3.13 eV 397 nm f=1.6388
S_0-S_{10}		
	3.23 eV 384 nm f=0.0074	3.14 eV 394 nm f=0.0000

[a] The negative density (blue) represents the hole, and the positive density (red) represent the electron. Calculated excitation energy and oscillator strength (f) are listed in the table. The detected absorption maximums are also listed in the corresponding table in bold type. The density data shown in this table were obtained by using ZINDO method.

Table S3. Calculated Vibrational Frequencies and Huang-Rhys Factors of the **Chromophore B**.

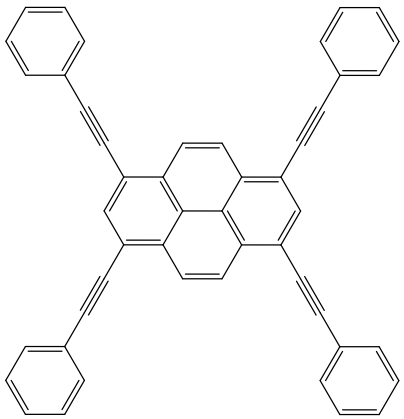
The Molecular Model for the Core Structure



Mode	Frequencies (cm^{-1})	Huang-Rhys Factors
1	55.287	1.84E-06
2	149.38	2.31E-06
3	215.35	3.30E-05
4	223.86	0.20403
5	275.42	6.86E-07
6	291.44	5.23E-14
7	375.63	2.73E-07
8	388.4	0.5417
9	414.46	0.06128
10	451.82	1.34E-07
11	529.54	2.82E-05
12	535.61	8.61E-07
13	608.26	0.01973
14	624.73	1.67E-06
15	673.99	8.00E-08
16	741.91	0.00127
17	794.04	9.56E-06
18	816.86	3.26E-07
19	832.83	0.10919
20	854.47	3.31E-07
21	897.16	4.54E-09

22	975.15	0.0107
23	1013.2	0.02424
24	1114.2	0.00332
25	1135.4	0.03306
26	1193.1	0.00431
27	1232.2	0.03193
28	1263.2	0.34098
29	1301.4	0.00828
30	1324.5	0.04327
31	1394	0.10336
32	1434.7	2.41E-04
33	1465.4	0.03087
34	1483.1	0.08676
35	1516.6	2.60E-04
36	1566.7	0.62783
37	1600.9	0.04843
38	3176	0.05363
39	3183.6	0.00835
40	3187.5	0.00651
41	3204	0.00195
42	3214.2	0.01208
43	3253.3	4.59E-04
44	3277.2	0.15988
45	3854.5	0.0714

Table S4. Calculated Vibrational Frequencies and Huang-Rhys Factors of the **Chromophore C**.

The Molecular Model for the Core Structure		
Mode	Frequencies (cm^{-1})	Huang-Rhys Factors
1	8.5587	1.69E-05
2	9.3155	2.18E-06
3	9.6844	1.48E-08
4	9.8053	8.02E-07
5	9.9318	2.37E-06
6	16.194	0.40362
7	16.838	7.56E-08
8	17.304	4.11E-08
9	19.852	3.35E-08
10	34.279	2.42E-08
11	37.921	4.38E-08
12	45.036	5.11E-08
13	76.136	3.26E-08
14	80.746	1.63E-09
15	102.2	6.52E-09
16	103.89	4.91E-08

17	107.38	0.00522
18	115.98	1.93E-09
19	122.51	1.23E-07
20	127.57	9.68E-10
21	137.62	6.28E-08
22	174.3	3.72E-04
23	197.76	7.32E-08
24	216.67	5.66E-10
25	222.17	1.53E-08
26	228.5	2.10E-08
27	232.28	1.28E-10
28	248.32	2.73E-07
29	270.75	3.05E-11
30	306.24	5.56E-10
31	309.55	1.14E-09
32	311.96	1.23E-10
33	316.26	1.11E-08
34	376.39	5.06E-08
35	390.11	0.33976
36	414.2	2.08E-10
37	419.3	6.36E-09
38	419.3	3.32E-09
39	419.31	1.91E-10
40	419.31	9.64E-12
41	421.93	2.21E-08

42	442.41	8.57E-09
43	445.81	2.58E-09
44	452.81	4.58E-09
45	462.81	0.02349
46	482.75	1.08E-08
47	487.39	1.02E-08
48	509.43	3.69E-08
49	521.97	4.63E-09
50	529.04	1.32E-07
51	530.43	2.60E-10
52	533.29	5.79E-08
53	547.09	9.46E-04
54	551.57	1.32E-09
55	551.75	2.66E-07
56	561.66	1.34E-08
57	564.2	6.64E-12
58	566.05	4.90E-08
59	569.86	8.73E-04
60	587.24	1.16E-08
61	603.75	1.15E-09
62	612.65	5.39E-12
63	641.57	6.75E-08
64	642.96	4.03E-08
65	643.33	2.13E-05
66	643.4	1.87E-08

67	655.72	8.86E-10
68	671.4	1.37E-09
69	674.04	5.30E-09
70	675.21	9.60E-09
71	675.34	3.92E-04
72	713.02	1.13E-10
73	716.85	2.15E-08
74	716.93	4.04E-08
75	716.96	2.08E-09
76	717.05	2.90E-08
77	727.53	4.44E-10
78	737.25	1.08E-07
79	745.98	1.39E-08
80	749.34	1.89E-08
81	789.11	1.47E-08
82	789.19	3.27E-08
83	789.24	2.38E-08
84	789.37	2.00E-09
85	798.28	1.19E-09
86	806.24	0.00468
87	828.63	7.47E-10
88	840.15	1.48E-10
89	860.48	1.85E-09
90	869.82	8.33E-10
91	873.91	7.29E-10

92	874.14	1.13E-07
93	874.21	9.37E-10
94	874.45	5.34E-08
95	875.76	1.46E-08
96	915.41	4.79E-08
97	940.33	7.26E-11
98	940.43	2.79E-10
99	952.19	1.35E-09
100	952.27	3.09E-08
101	952.29	1.14E-09
102	952.41	8.68E-10
103	999.34	5.64E-09
104	999.36	3.45E-09
105	999.38	7.69E-10
106	999.39	9.53E-10
107	1021.3	2.75E-09
108	1023.3	6.29E-12
109	1025.5	3.12E-08
110	1025.5	7.84E-09
111	1025.5	5.13E-09
112	1025.6	1.77E-12
113	1027.5	0.00894
114	1029.2	1.16E-08
115	1029.3	8.50E-07
116	1029.3	1.97E-09

117	1029.5	9.03E-04
118	1033.4	1.17E-09
119	1068.5	4.84E-08
120	1069.6	2.27E-07
121	1071.2	1.53E-04
122	1072.8	6.66E-11
123	1110.3	1.50E-07
124	1120.3	2.73E-07
125	1120.3	4.44E-08
126	1120.4	7.40E-04
127	1120.4	9.61E-08
128	1169.6	1.40E-10
129	1185.5	6.01E-08
130	1193.1	0.00123
131	1193.1	5.55E-07
132	1193.1	8.20E-08
133	1193.1	2.97E-08
134	1195.7	2.33E-08
135	1202.1	0.01387
136	1213.7	0.00438
137	1213.9	3.47E-08
138	1214.2	4.67E-08
139	1214.8	2.25E-08
140	1235.3	0.07892
141	1237.9	4.18E-09

142	1240.2	1.29E-09
143	1254.4	7.50E-08
144	1310	1.09E-07
145	1321.8	8.09E-09
146	1330.2	0.13977
147	1331.1	6.40E-08
148	1331.2	0.0015
149	1331.2	1.78E-06
150	1331.2	4.25E-08
151	1335.7	2.18E-10
152	1367.1	7.21E-06
153	1367.1	6.59E-07
154	1367.1	1.34E-07
155	1367.2	0.00294
156	1378	4.23E-08
157	1404.3	2.35E-09
158	1424.8	0.22094
159	1441.9	3.37E-08
160	1449.8	0.00991
161	1456.7	3.74E-09
162	1457.2	1.47E-09
163	1504.8	0.00172
164	1504.8	1.33E-06
165	1504.8	1.23E-06
166	1504.8	9.68E-08

167	1533	2.64E-08
168	1554.7	2.45E-07
169	1555.7	2.16E-07
170	1562.2	5.50E-04
171	1563.1	3.06E-07
172	1574.6	0.04473
173	1584.2	4.97E-08
174	1586.8	2.04E-12
175	1627	6.04E-09
176	1664.7	1.42E-08
177	1664.7	1.40E-09
178	1664.8	3.26E-05
179	1664.8	7.26E-07
180	1673.9	3.80E-10
181	1693.9	1.16E-06
182	1697.4	0.02058
183	1697.5	1.75E-08
184	1698.2	3.97E-10
185	1703.1	1.19E-06
186	1714	0.27436
187	2366	1.17E-08
188	2366.2	8.50E-09
189	2367.5	0.01035
190	2368.8	8.10E-09
191	3209.1	7.51E-07

192	3209.1	4.06E-07
193	3209.1	2.10E-07
194	3209.2	8.75E-05
195	3217.8	1.57E-04
196	3217.8	8.62E-05
197	3217.8	8.22E-06
198	3217.8	5.31E-08
199	3227.6	1.39E-04
200	3227.6	1.19E-07
201	3227.6	3.12E-08
202	3227.6	1.03E-11
203	3230.8	3.04E-10
204	3230.9	2.93E-10
205	3235	3.33E-05
206	3235	1.42E-06
207	3235	6.81E-07
208	3235	8.11E-10
209	3239.8	0.00118
210	3239.8	1.20E-06
211	3239.8	1.68E-07
212	3239.8	3.17E-08
213	3244.9	4.11E-10
214	3245	1.71E-06
215	3246.6	7.83E-09
216	3246.7	1.42E-04

Table S5. Molecular Orbitals Involved in $S_0 \rightarrow S_1$ Transition of **Chromophore B**.

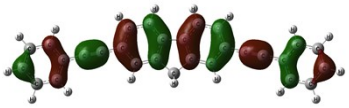
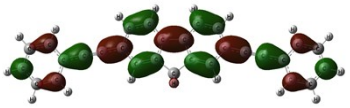
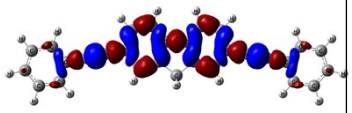
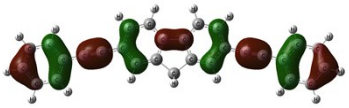
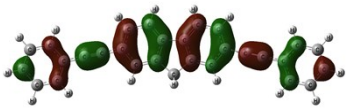
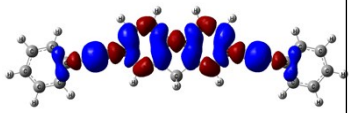
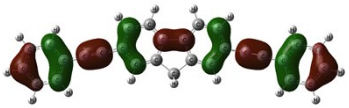
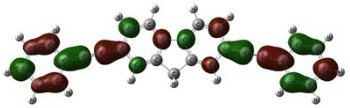
Method	Oscillator Strength	Coefficient	Hole	Density	CDD
TD-CAM-B3LYP	f=2.3520	0.66373	 HOMO	 LUMO	
		0.19712	 HOMO-1	 LUMO+1	
ZINDO	f=1.7538	0.61720	 HOMO	 LUMO	
		-0.24271	 HOMO-1	 LUMO+1	

Table S6. Molecular Orbitals Involved in $S_0 \rightarrow S_1$ Transition of **Chromophore C**.

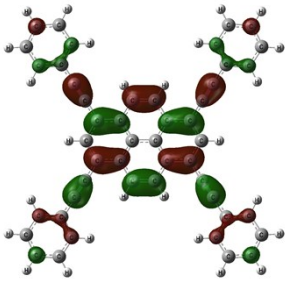
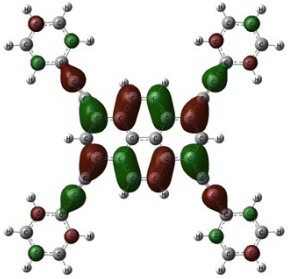
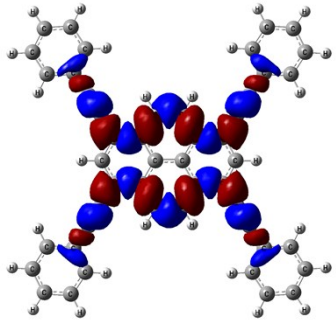
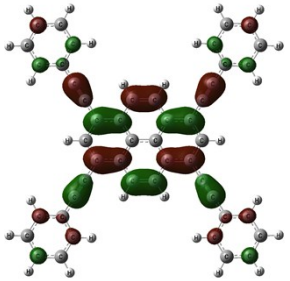
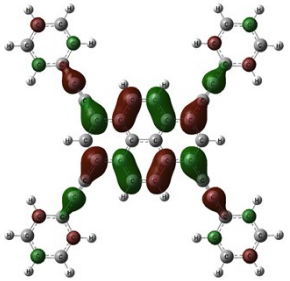
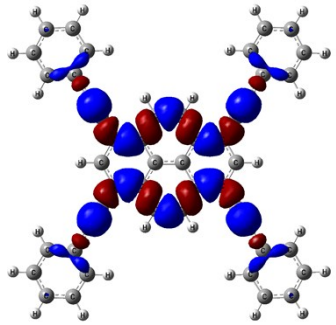
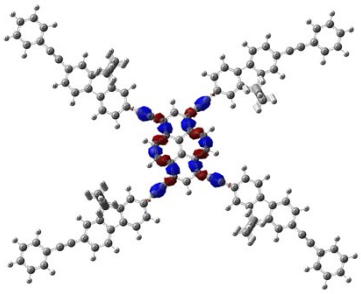
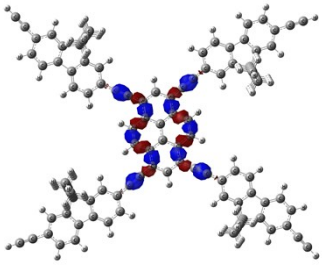
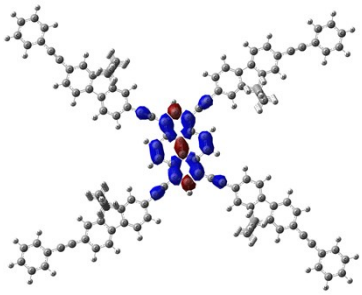
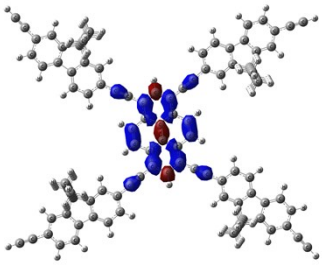
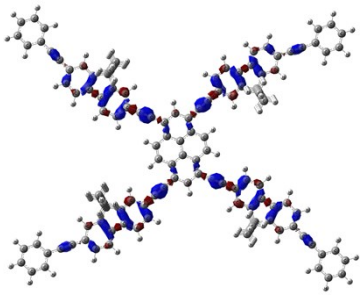
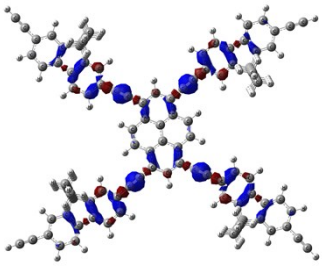
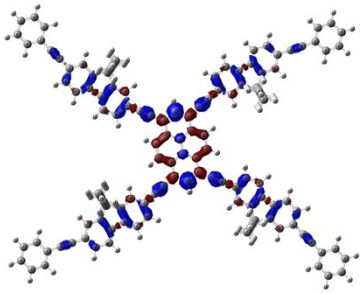
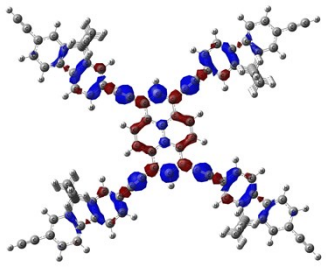
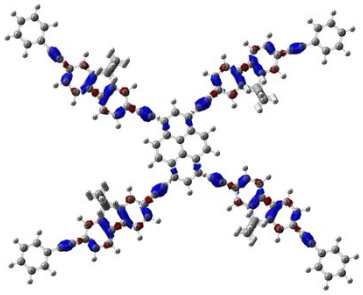
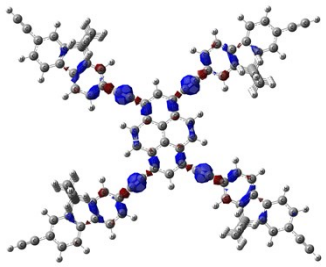
Method	Oscillator Strength	Coefficient	Hole	Density	CDD
TD-CAM-B3LYP	f=1.3716	0.68963	 HOMO	 LUMO	
ZINDO	f=1.3357	0.66492	 HOMO	 LUMO	

Table S7. Calculated Excited States Charge Difference density (CDD) of T1.[a]

Transition	M 1	M 2
S_0-S_1		
	2.4998 eV 495.97 nm f=1.8455	2.5109 eV 493.79 nm f=1.6823
S_0-S_2		
	3.0537 eV 406.02 nm f=0.6980	3.0590 eV 405.31 nm f=0.2517
S_0-S_3		

	3.1535 eV 393.17 nm f=0.0000	3.2386 eV 382.83 nm f=0.0000
S_0-S_4		
	3.1618 eV 392.13 nm f=4.5559	3.2441 eV 382.18 nm f=3.7934
S_0-S_5		
	3.3358 eV 371.67 nm f=0.0000	3.4237 eV 362.13 nm f=0.0000

[a] The negative density (blue) represents the hole, and the positive density (red) represent the electron. Calculated excitation energy and oscillator strength (f) are listed in the table. The detected absorption maximums are also listed in the corresponding table in bold type. The density data shown in this table were obtained by using ZINDO method.