Electronic Supplementary Material (ESI) for RSC Advances

Supplementary Information

Sterically Congested Pyrrole-Fused Tetrathiafulvalene Decamers as Highly Conductive Amorphous Molecular Materials

Masayoshi Takase,* Naofumi Yoshida, Tomoyuki Narita, Takashi Fujio, Tohru Nishinaga, and Masahiko Iyoda*

Department of Chemistry, Graduate School of Science and Engineering, Tokyo Metropolitan University, Hachioji, Tokyo 192-0397, Japan,

E-mail: mtakase@tmu.ac.jp, iyoda@tmu.ac.jp

Contents

S1. Material and methods

^{1}H and ^{13}C NMR spectra were recorded on Bruker 500 spectrometer with use of tetramethylsilane proton or carbon signal as an internal standard. Electron impact (EI) mass spectra and laser desorption ionization time-of-flight (LDI-TOF) mass spectra were obtained on SHIMADZU GC-MS QP2020 and AXIMA-CFR, respectively. Melting points were determined with Yanako MP-500D and not corrected. Elemental analyses were performed with Exeter Analytical, Inc. CE-440F. Column chromatography was carried out using Merck silica gel 60, Daiso silica gel 1001W, or neutral alumina activity II-III, 70-230 mesh ASTM. Gel permeation chromatography (GPC) was performed using a JAI model LC-908 recycling preparative HPLC equipped with JAIGEL-1H-40 and -2H-40 columns (40 x 600 mm) with toluene as eluent. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) was carried out with Rigaku DSC8230L under nitrogen atmosphere. Absorption spectra were recorded on SHIMADZU UV-Vis-NIR scanning spectrophotometer (Model UV-3101-PC). Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) measurements were performed on BAS-ALS620B electrochemical analyzer using a standard three-electrode cell consisting of Pt working electrodes, a Pt wire counter electrode, and a Ag/$AgNO_3$ reference electrode under nitrogen atmosphere. The potentials were calibrated with ferrocene as an external standard. Atomic force field microscopy (AFM) and scanning electronic microscopy (SEM) measurements were carried out with KEYENCE, Nanoscale Hybrid Microscope VN-8000 (tapping mode) and KEYENCE VE-9800, respectively. Electric conductivity measurements were performed with Advantest R6551 Digital Multimeter. All reactions were carried out under nitrogen atmosphere. THF was freshly distilled from sodium benzophenone ketyl before use, and other solvents were purified with standard methods.

Synthetic Methods

Decakis[2-(4,5-bis(butylthio)-1,3-dithiol-2-ylidene)-(1,3)-dithiolo[4,5-*c*]-*N*-pyrrolyl]biphenyl (4b)
To a DMF-THF (5 + 5 mL) solution of **6** (303 mg 0.72 mmol) was adeded NaH (60% oil dispersion, 33 mg, 0.83 mmol) at 0 °C. After stirring for 30 min at the same temperature, decafluorobiphenyl (12 mg, 0.36 mmol) was added. The reaction mixture was allowed to warm to room temperature over 9 hours, and then it was heated up to 70 °C and stirred for 3 hours. After addition of H_2O, the aqueous phase was extracted by THF, and then combined organic phase was washed with brine, and dried over $MgSO_4$. Concentration in vacuo gave a dark oil, which was subjected to column chromatography (Al_2O_3; eluent, CH_2Cl_2) and GPC (eluent, toluene), and re-crystalized from CH_2Cl_2 and hexane to give **4b** as a dark-yellow solid in 44% yield (67 mg, 0.016 mmol). dec. > 226 °C; ^{1}H NMR (500 MHz,

$CDCl_3$) δ 5.98 (s, 4H), 5.86 (s, 8H), 5.65 (s, 8H), 2.84-2.79 (t, J = 7.3 Hz, 40H), 1.68-1.58 (m, 40H), 1.44-1.39 (m, 40H), 0.97-0.89 (m, 60H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 132.35, 127.64, 127.52, 126.56, 125.17, 124.96, 124.42, 117.70, 117.46, 115.18, 114.86, 112.27, 112.15. 111.99, 111.72, 111.66, 36.04, 35.99, 31.76, 21.73, 21.70, 21.67, 13.68, 13.64; UV-vis (CH_2Cl_2/CH_3CN 2:1) λ_{max} nm (log ε) 298 (4.65), 322 (4.59), 370 (4.21); LDI-TOF-MS: calcd for MH^+, $C_{172}H_{200}N_{10}S_{60}$: 4329.9; found 4331.5. Anal. Calcd for $C_{172}H_{200}N_{10}S_{60}$: C, 47.69; H, 4.65; N, 3.23. Found: C, 47.98; H, 4.72; N, 3.20.

Decakis(*N*-pyrrolyl)biphenyl (5)

To a DMF (20 mL) solution of pyrrole (679 mg 10.0 mmol) was adeded NaH (60% oil dispersion, 420 mg, 10.5 mmol) at 0 °C. After stirring for 30 min at the same temperature, decafluorobiphenyl (167 mg, 0.50 mmol) was added. The reaction mixture was heated up to 80 °C and stirred for overnight. After addition of H_2O, the aqueous phase was extracted by ether, and then combined organic phase was washed with brine, and dried over $MgSO_4$. Concentration in vacuo gave a pale-yellow solid, which was subjected to column chromatography (SiO_2; eluent, Hexane: CH_2Cl_2 = 2: 3) and crystalized from CH_2Cl_2 and hexane to give **5** as colorless prisms in 96% yield (378 mg, 0.47 mmol). dec. > 311 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.08 (dd, J = 2.1, 2.1 Hz, 4H), 6.03-5.98 (m, 28H), 5.96 (dd, J = 2.2, 2.2 Hz, 8H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 136.89, 136.46, 133.53, 127.57, 121.46, 120.87(2C), 110.55, 110.40, 109.86; EI-MS: calcd for M^+, $C_{52}H_{40}N_{10}$: 804.3; found 804.; Anal. Calcd for $C_{52}H_{40}N_{10}$: C, 77.59; H, 5.01; N, 17.40. Found: C, 77.20; H, 4.74; N, 17.22.

S2. ^{1}H and ^{13}C NMR spectra

Figure S2-1. ^{1}H NMR of **4b** ($CDCl_3$, 500 MHz)

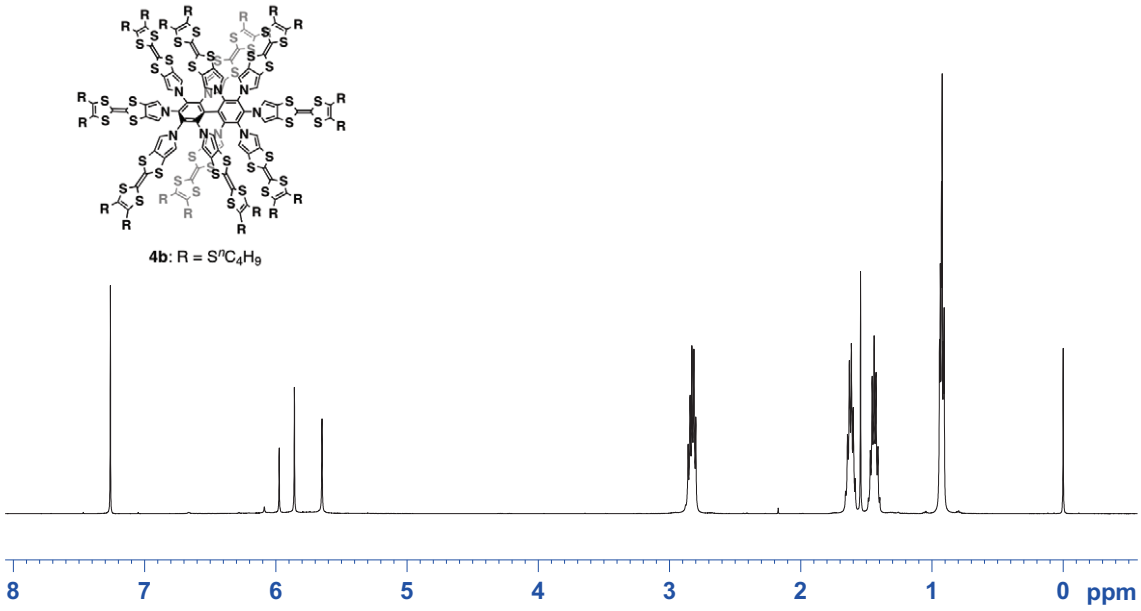


Figure S2-2. ^{13}C NMR of **4b** ($CDCl_3$, 125 MHz)

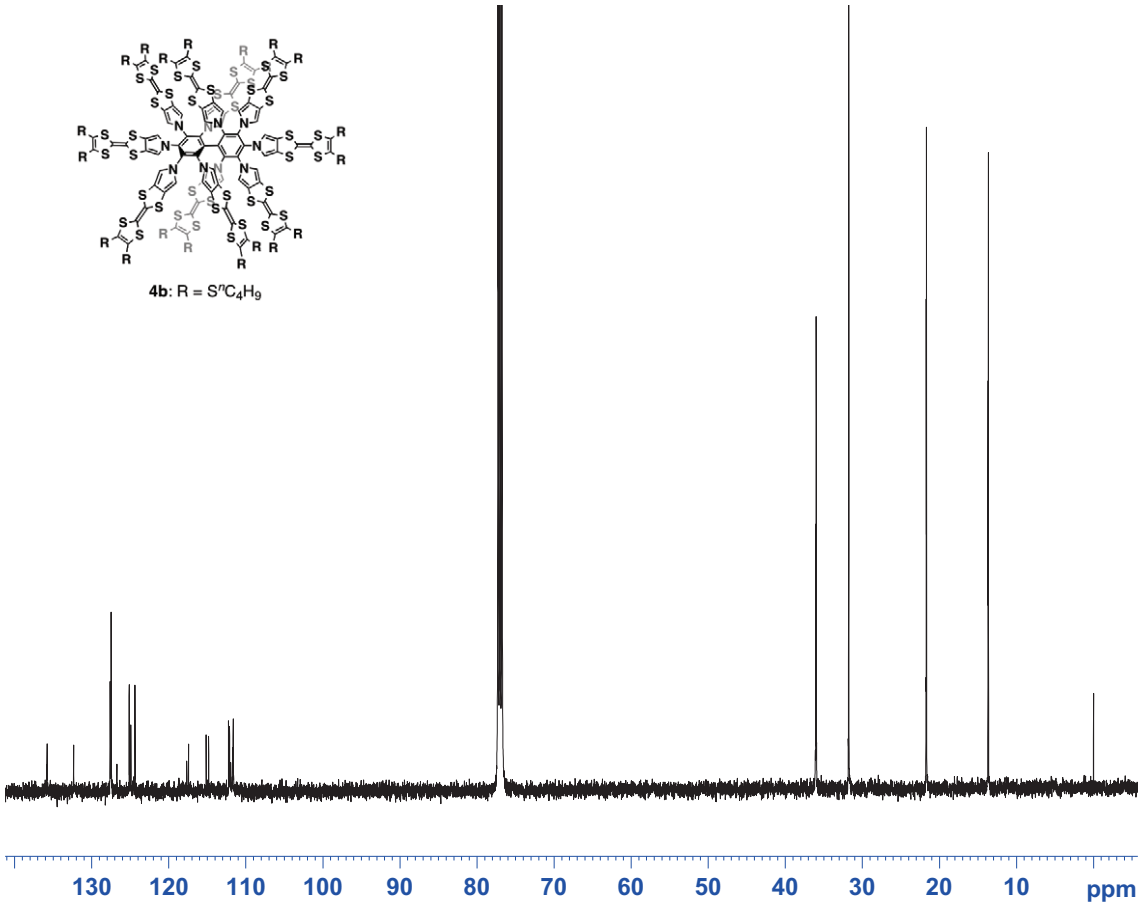


Figure S2-3. ^{1}H NMR of **5** ($CDCl_3$, 500 MHz)

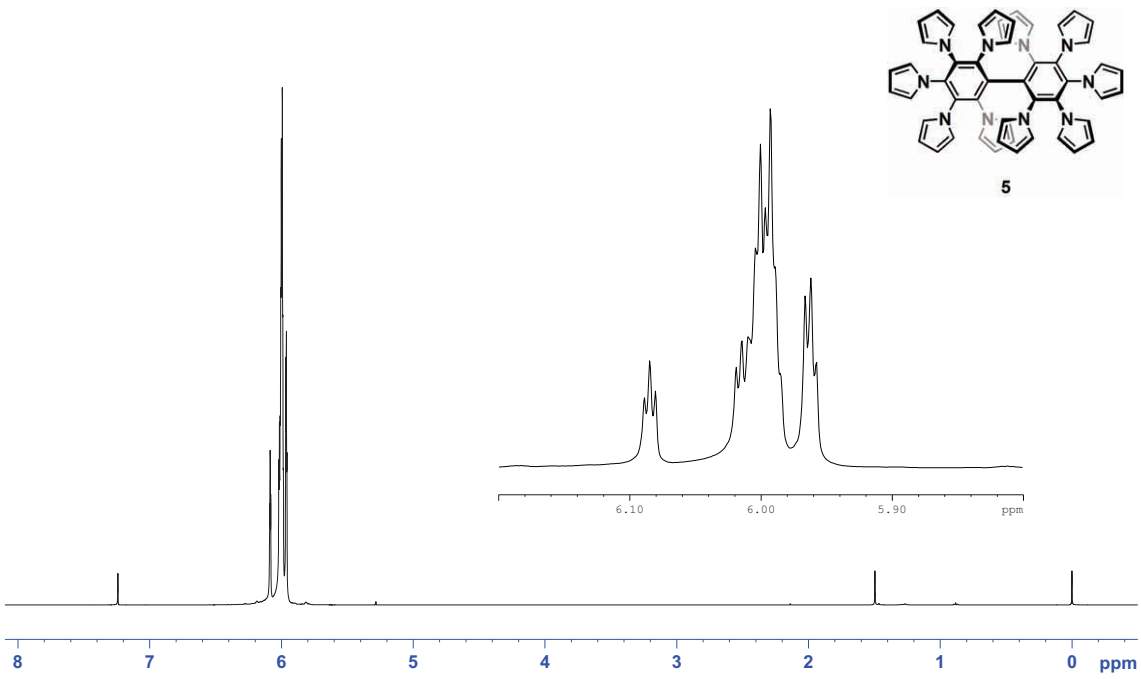
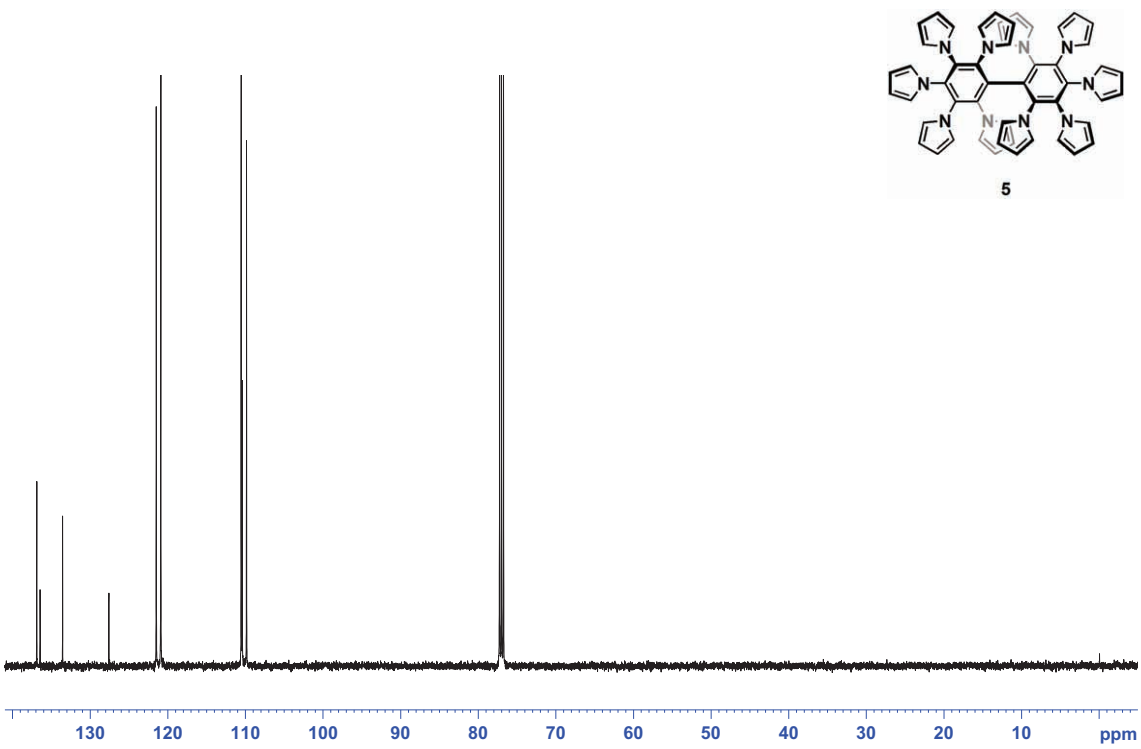
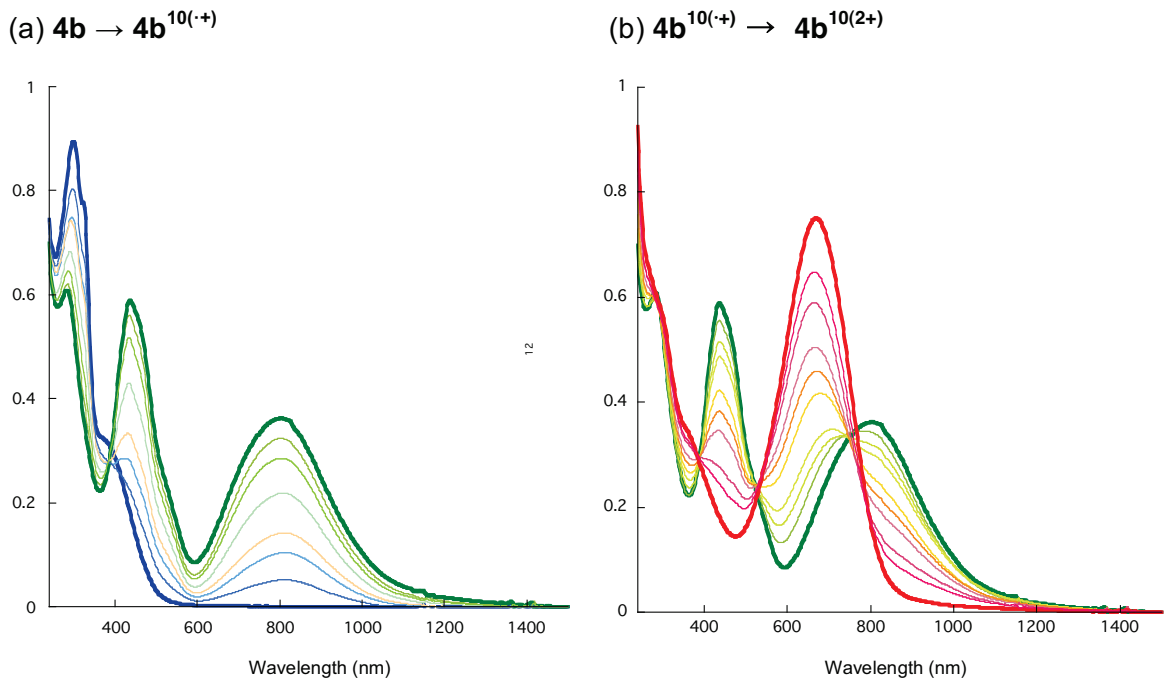


Figure S2-4. ^{13}C NMR of **5** ($CDCl_3$, 125 MHz)



S3. Chemical oxidations of 4b

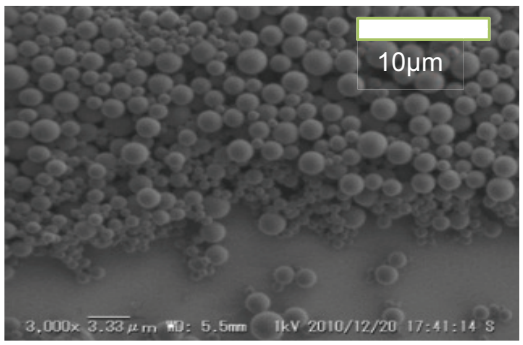
Figure S3-1. Absorption spectra of **4b** (0.02 mM) in the presence of various amount of oxidant, $Fe(ClO_4)_3 \bullet 6H_2O$ in a mixture of CH_2Cl_2 and CH_3CN (2:1, v/v) at room temperature.



S4. XRD patterns and SEM images of self-assembled 4b and their conductivities

Figure S4-1. (a) SEM images and (b) XRD patterns of **4b-particle**. For SEM measurements, the samples were prepared by casting a suspension of nanostructures onto a cleaned Si wafer, followed by drying. The conductivities for these assembled structures were *measured by two-probe technique* using fine gold wires (10 μm diameter) attached to the pellets made of fibers, particles or films with carbon paste. Thickness of the pellets and spin coat films were estimated by AFM with tapping mode. The values are averages of two measurements by preparing different samples.

(a)



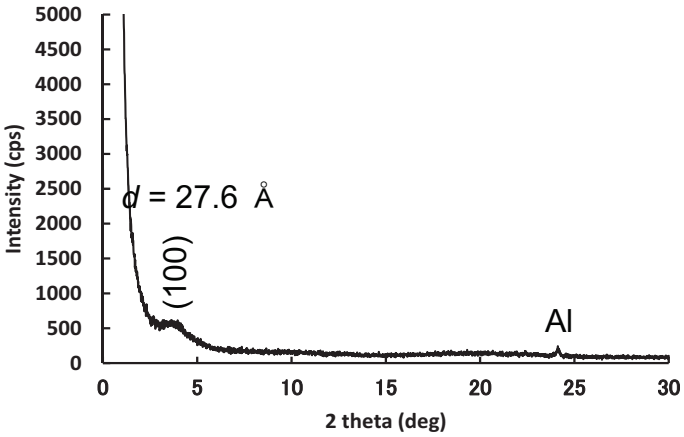
4b-particle: 5 mg/ml

(CH_2Cl_2 : hexane = 1:4, v/v)

δ_{rt} **= 7.8 x 10^{-2} S/cm**

(after I_2 dope)

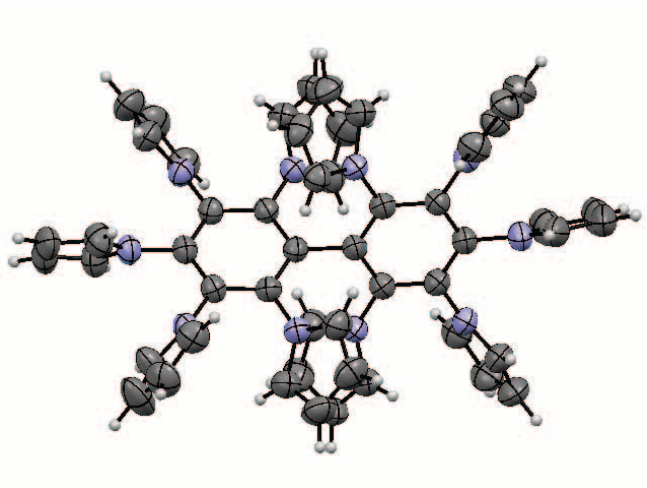
(b)



S5. Single crystal structure of 5

X-ray data were taken on a Bruker Smart APEX diffractometer equipped with a CCD area detector with graphite-monochromated MoKa. radiation (λ = 0.71073 Å). The structure was solved by direct methods (SHELXTL) and refined by the full-matrix least-squares method on F^2 (SHELXL-97). Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were placed using AFIX instructions.

Figure S5-1. ORTEP drawings of **5.**



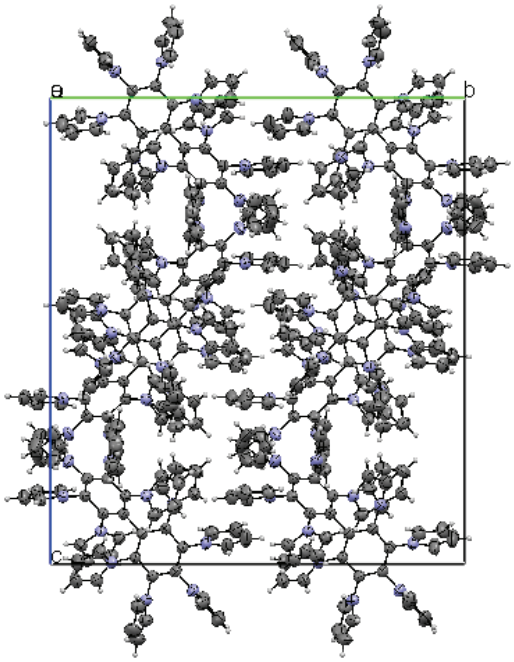


Table S5-1. Crystal data and structure refinement for **5.**

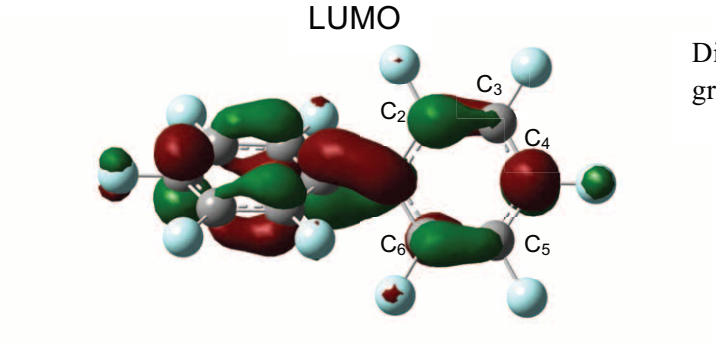
Identification code	**5**	
Empirical formula	C52 H40 N10	
Formula weight	804.94	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	orthorhombic	
Space group	Pbca	
Unit cell dimensions	a = 14.853(3) Å	α = 90°.
	b = 22.747(3) Å	β = 90°.
	c = 25.640(4) Å	γ = 90°.
Volume	8663(2) $Å^3$	
Z	8	
Density (calculated)	1.234 Mg/m^3	
Absorption coefficient	0.076 mm^{-1}	
F(000)	3376	
Crystal size	0.40 x 0.20 x 0.30 mm^3	
Theta range for data collection	1.59 to 23.28°.	
Index ranges	-16<=h<=16, -25<=k<=22, -28<=l<=27	
Reflections collected	36688	
Independent reflections	6235 [R(int) = 0.0468]	
Completeness to theta = 23.28°	99.8 %	
Absorption correction	Empirical	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6235 / 0 / 559	
Goodness-of-fit on F^2	1.035	
Final R indices [I>2sigma(I)]	R1 = 0.0431, wR2 = 0.1172	
R indices (all data)	R1 = 0.0686, wR2 = 0.1430	
Largest diff. peak and hole	0.151 and -0.214 e.$Å^{-3}$	

S6. DFT calculations of decafluorobiphenyl and 4a[1]

The optimizations were performed with D_2 symmetry for **4a** at the RB3LYP/6-31G (d) level of theory.

Figure S6-1. (a) LUMO of decafluorobiphenyl, and (b) optimized structure and (c) HOMO and LUMOs of **4a**.

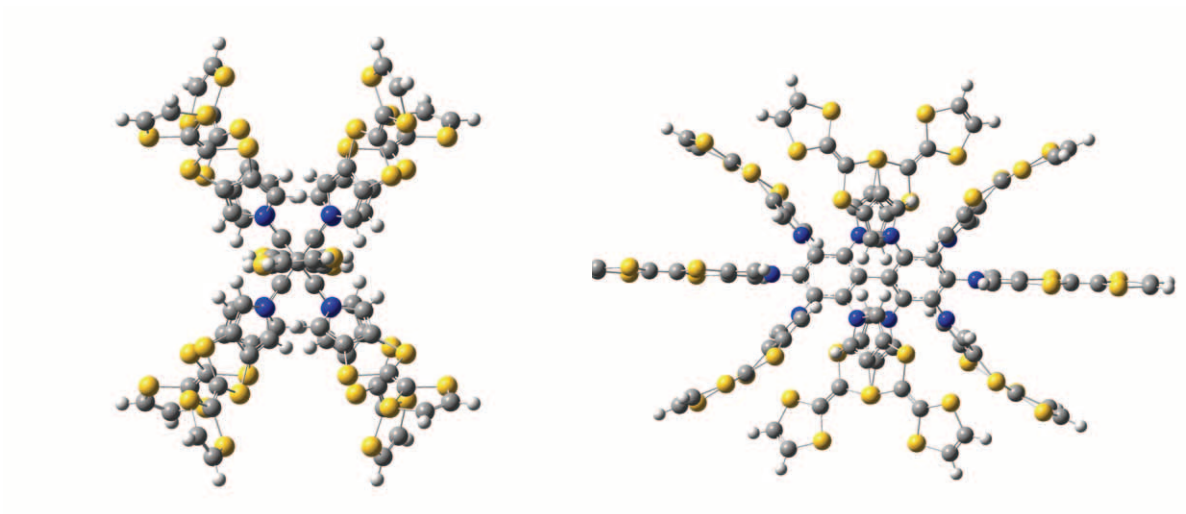
(a) LUMO of decafluorobiphenyl



Dihedral angle between pentafluorophenyl groups: **54°**

According to the LUMO of decafluorobiphenyl, the orbitals are preferentially located at the *ortho*- and *para*-positions (C_2, C_2', C_4, and C_4'), indicating that the S_NAr reactions at these positions are favorable. However, once less hindered positions of the biphenyl moiety, *i.e.*, C_3, C_3', C_4, C_4', C_5, and C_5', are substituted, complete substitution at the *ortho*-positions, *i.e.*, C_2, C_2', C_6, and C_6', is hampered in the case with bulky substituent **6**, even at higher temperatures.

(b) Optimized structure of **4a**



Dihedral angle between the phenyl groups: **71°**

(c) Molecular orbitals of **4a**

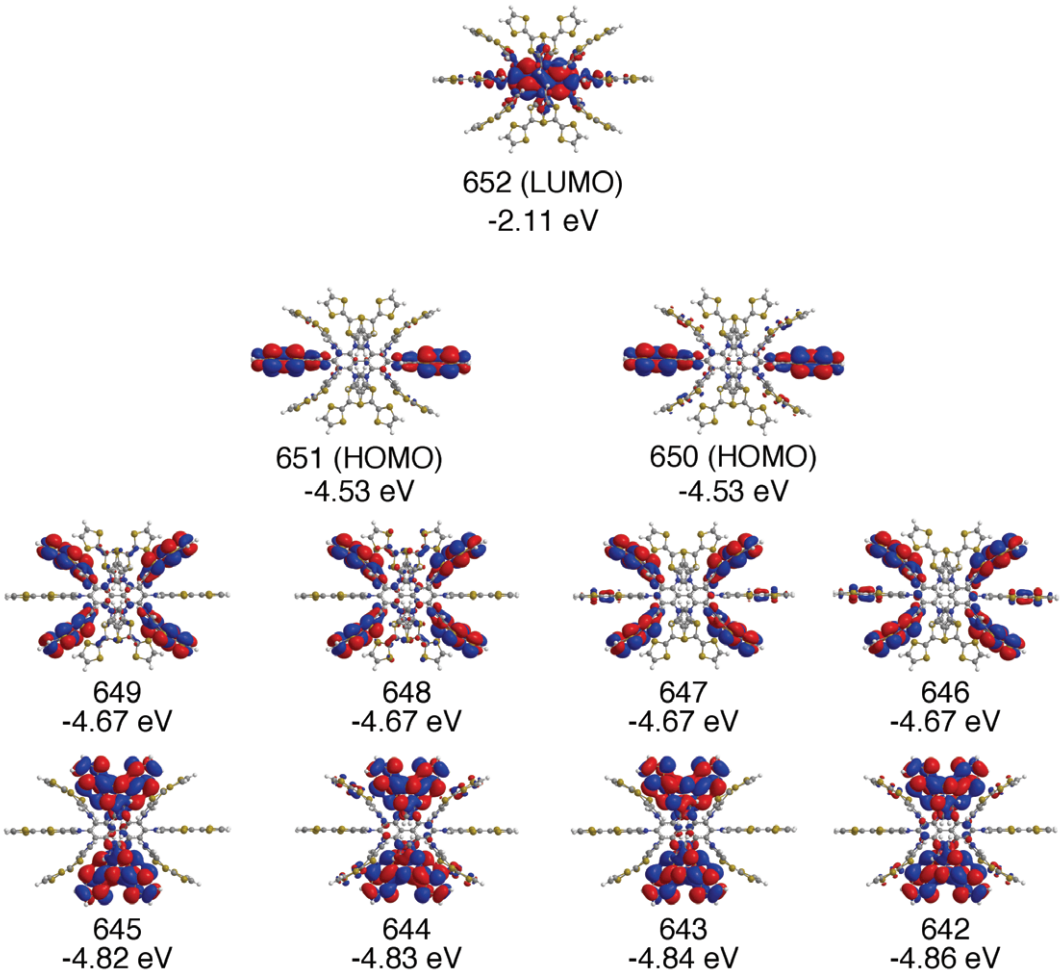


Table S8-1. Atomic coordination of **4a** (D_2 symmetry)

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	0.000000	0.000000	0.750307
2	6	-0.711951	0.990036	1.462852
3	6	-0.735648	0.974842	2.875487
4	6	0.000000	0.000000	3.579419
5	6	0.735648	-0.974842	2.875487
6	6	0.711951	-0.990036	1.462852
7	6	0.000000	0.000000	-0.750307
8	6	-0.711951	-0.990036	-1.462852
9	6	-0.735648	-0.974842	-2.875487
10	6	0.000000	0.000000	-3.579419
11	6	0.735648	0.974842	-2.875487
12	6	0.711951	0.990036	-1.462852
13	7	0.000000	0.000000	4.993587
14	6	-1.132254	-0.116620	5.797075
15	6	1.132254	0.116620	5.797075
16	6	-0.709424	-0.074009	7.100603
17	1	-2.117344	-0.189348	5.363811
18	6	0.709424	0.074009	7.100603
19	1	2.117344	0.189348	5.363811
20	16	-1.515265	-0.154121	8.660325
21	16	1.515265	0.154121	8.660325
22	6	0.000000	0.000000	9.609790
23	6	0.000000	0.000000	10.959239
24	16	-1.490085	-0.158032	11.936945
25	16	1.490085	0.158032	11.936945
26	7	-1.480896	1.942837	3.589179
27	6	-0.959351	2.839772	4.519266
28	6	-2.857057	2.132919	3.480626
29	6	-2.004756	3.593955	4.985394
30	1	0.089035	2.830833	4.773372
31	6	-3.195573	3.149732	4.334979
32	1	-3.448049	1.545139	2.795797
33	16	-2.163046	4.943186	6.106949
34	16	-4.685550	4.004543	4.723751
35	6	-3.954683	4.867697	6.115152
36	6	-4.700099	5.454996	7.075027
37	16	-3.994850	6.354003	8.448513
38	16	-6.486660	5.420473	7.084857
39	7	1.480896	-1.942837	3.589179
40	6	0.959351	-2.839772	4.519266
41	6	2.857057	-2.132919	3.480626
42	6	2.004756	-3.593955	4.985394
43	1	-0.089035	-2.830833	4.773372
44	6	3.195573	-3.149732	4.334979
45	1	3.448049	-1.545139	2.795797
46	16	2.163046	-4.943186	6.106949
47	16	4.685550	-4.004543	4.723751
48	6	3.954683	-4.867697	6.115152
49	6	4.700099	-5.454996	7.075027
50	16	3.994850	-6.354003	8.448513
51	16	6.486660	-5.420473	7.084857
52	7	1.405379	-2.023539	0.776464
53	6	1.248528	-3.383926	1.032351
54	6	2.390561	-1.855898	-0.201009
55	6	2.118789	-4.061884	0.221062
56	1	0.523328	-3.734438	1.748412
57	6	2.838852	-3.101965	-0.551542
58	1	2.672142	-0.881833	-0.560967
59	16	2.527910	-5.757769	-0.032883
60	16	4.060327	-3.721791	-1.660142
61	6	3.471388	-5.411777	-1.517289
62	6	3.751186	-6.355101	-2.441672
63	16	3.198802	-8.047977	-2.308064
64	16	4.716419	-6.031281	-3.909317
65	7	-1.405379	2.023539	0.776464
66	6	-1.248528	3.383926	1.032351
67	6	-2.390561	1.855898	-0.201009
68	6	-2.118789	4.061884	0.221062
69	1	-0.523328	3.734438	1.748412
70	6	-2.838852	3.101965	-0.551542
71	1	-2.672142	0.881833	-0.560967
72	16	-2.527910	5.757769	-0.032883
73	16	-4.060327	3.721791	-1.660142
74	6	-3.471388	5.411777	-1.517289
75	6	-3.751186	6.355101	-2.441672
76	16	-3.198802	8.047977	-2.308064
77	16	-4.716419	6.031281	-3.909317
78	7	-1.405379	-2.023539	-0.776464
79	6	-2.390561	-1.855898	0.201009
80	6	-1.248528	-3.383926	-1.032351
81	6	-2.838852	-3.101965	0.551542
82	1	-2.672142	-0.881833	0.560967
83	6	-2.118789	-4.061884	-0.221062
84	1	-0.523328	-3.734438	-1.748412
85	16	-4.060327	-3.721791	1.660142
86	16	-2.527910	-5.757769	0.032883
87	6	-3.471388	-5.411777	1.517289
88	6	-3.751186	-6.355101	2.441672
89	16	-4.716419	-6.031281	3.909317
90	16	-3.198802	-8.047977	2.308064
91	7	-1.480896	-1.942837	-3.589179
92	6	-2.857057	-2.132919	-3.480626
93	6	-0.959351	-2.839772	-4.519266
94	6	-3.195573	-3.149732	-4.334979
95	1	-3.448049	-1.545139	-2.795797
96	6	-2.004756	-3.593955	-4.985394
97	1	0.089035	-2.830833	-4.773372
98	16	-4.685550	-4.004543	-4.723751
99	16	-2.163046	-4.943186	-6.106949
100	6	-3.954683	-4.867697	-6.115152
101	6	-4.700099	-5.454996	-7.075027
102	16	-6.486660	-5.420473	-7.084857
103	16	-3.994850	-6.354003	-8.448513
104	7	1.405379	2.023539	-0.776464
105	6	2.390561	1.855898	0.201009
106	6	1.248528	3.383926	-1.032351
107	6	2.838852	3.101965	0.551542
108	1	2.672142	0.881833	0.560967
109	6	2.118789	4.061884	-0.221062
110	1	0.523328	3.734438	-1.748412
111	16	4.060327	3.721791	1.660142
112	16	2.527910	5.757769	0.032883
113	6	3.471388	5.411777	1.517289
114	6	3.751186	6.355101	2.441672
115	16	4.716419	6.031281	3.909317
116	16	3.198802	8.047977	2.308064
117	7	1.480896	1.942837	-3.589179
118	6	2.857057	2.132919	-3.480626
119	6	0.959351	2.839772	-4.519266
120	6	3.195573	3.149732	-4.334979
121	1	3.448049	1.545139	-2.795797
122	6	2.004756	3.593955	-4.985394
123	1	-0.089035	2.830833	-4.773372
124	16	4.685550	4.004543	-4.723751
125	16	2.163046	4.943186	-6.106949
126	6	3.954683	4.867697	-6.115152
127	6	4.700099	5.454996	-7.075027
128	16	6.486660	5.420473	-7.084857

129	16	3.994850	6.354003	-8.448513
130	7	0.000000	0.000000	-4.993587
131	6	1.132254	-0.116620	-5.797075
132	6	-1.132254	0.116620	-5.797075
133	6	0.709424	-0.074009	-7.100603
134	1	2.117344	-0.189348	-5.363811
135	6	-0.709424	0.074009	-7.100603
136	1	-2.117344	0.189348	-5.363811
137	16	1.515265	-0.154121	-8.660325
138	16	-1.515265	0.154121	-8.660325
139	6	0.000000	0.000000	-9.609790
140	6	0.000000	0.000000	-10.959239
141	16	1.490085	-0.158032	-11.936945
142	16	-1.490085	0.158032	-11.936945
143	6	6.637357	-6.108090	8.701781
144	1	7.635702	-6.178067	9.117603
145	6	5.523112	-6.525692	9.311337
146	1	5.487202	-6.982929	10.293237
147	6	-0.664730	-0.070735	13.490880
148	1	-1.280548	-0.136144	14.380265
149	6	0.664730	0.070735	13.490880
150	1	1.280548	0.136144	14.380265
151	6	-3.691082	-8.491290	3.942346
152	1	-3.434758	-9.488127	4.281596
153	6	-4.369705	-7.589841	4.659296
154	1	-4.744238	-7.748762	5.663711
155	6	-5.523112	6.525692	9.311337
156	1	-5.487202	6.982929	10.293237
157	6	-6.637357	6.108090	8.701781
158	1	-7.635702	6.178067	9.117603
159	6	-4.369705	7.589841	-4.659296
160	1	-4.744238	7.748762	-5.663711
161	6	-3.691082	8.491290	-3.942346
162	1	-3.434758	9.488127	-4.281596
163	6	3.691082	8.491290	3.942346
164	1	3.434758	9.488127	4.281596
165	6	4.369705	7.589841	4.659296
166	1	4.744238	7.748762	5.663711
167	6	5.523112	6.525692	-9.311337
168	1	5.487202	6.982929	-10.293237
169	6	6.637357	6.108090	-8.701781
170	1	7.635702	6.178067	-9.117603
171	6	-0.664730	0.070735	-13.490880
172	1	-1.280548	0.136144	-14.380265
173	6	0.664730	-0.070735	-13.490880
174	1	1.280548	-0.136144	-14.380265
175	6	-5.523112	-6.525692	-9.311337
176	1	-5.487202	-6.982929	-10.293237
177	6	-6.637357	-6.108090	-8.701781
178	1	-7.635702	-6.178067	-9.117603
179	6	4.369705	-7.589841	-4.659296
180	1	4.744238	-7.748762	-5.663711
181	6	3.691082	-8.491290	-3.942346
182	1	3.434758	-9.488127	-4.281596

S6. References

[1] Gaussian 03, Revision E.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, .; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. Gaussian, Inc., Wallingford CT, 2004.