

## ***Electronic Supplementary Information***

### **D- $\pi$ -A-type fluorinated tolans with a dphenylamino group: Crystal polymorphism formation and photophysical behavior**

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## 1. Experimental

### 1.1. General methods

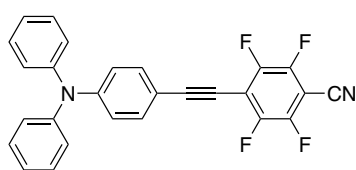
$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were obtained with a Bruker AVANCE III 400 NMR spectrometer ( $^1\text{H}$ : 400 MHz and  $^{13}\text{C}$ : 100 MHz) in chloroform-*d* ( $\text{CDCl}_3$ ) solution and the chemical shifts are reported in parts per million (ppm) using the residual proton in the NMR solvent.  $^{19}\text{F}$  NMR (376 MHz) spectra were obtained with a Bruker AVANCE III 400 NMR spectrometer in  $\text{CDCl}_3$  solution with hexafluorobenzene ( $\delta_{\text{F}} = 163$  ppm) as an internal standard. Infrared spectra (IR) were recorded in a KBr method with a JASCO FT/IR-4100 type A spectrometer; all spectra were reported in wavenumber ( $\text{cm}^{-1}$ ). High resolution mass spectra (HRMS) were recorded on a JEOL JMS-700MS spectrometer using fast atom bombardment (FAB) methods. All reactions were carried out using dried glassware with a magnetic stirrer bar. All chemicals were of reagent grade and where necessary were purified in the usual manner prior to use. Column chromatography was carried out on silica gel (Wakogel<sup>®</sup> 60N, 38-100  $\mu\text{m}$ ) and TLC analysis was performed on silica gel TLC plates (Merck, Silica gel 60F<sub>254</sub>).

### 1.2. Synthesis

#### Typical synthetic procedure for 2,3,5,6-tetrafluoro-4-[(4-(diphenylamino)phenyl)ethynyl]benzonitrile (**1**)

In a two-necked round-bottomed flask, equipped with a Teflon<sup>®</sup>-coated stirrer bar was placed 4-diphenylamino-phenyl acetylene (0.99 g, 3.7 mmol) and THF (36 mL) and cooled to 0 °C. To the resultant solution was added a solution of *n*-BuLi (1.6 mol L<sup>-1</sup>; 3.5 mL, 5.55 mmol) and the whole was stirred room temperature overnight. After being stirred at the temperature for 18 h, the resultant solution was poured into saturated aqueous  $\text{NH}_4\text{Cl}$  solution (30 mL). Crude product was extracted with EtOAc (30 mL, three times) and organic layer combined was washed with brine (once). The collected organic layer was dried over anhydrous  $\text{Na}_2\text{SO}_4$ , which was separated by filtration. The filtrate was evaporated in vacuo and subjected to silica-gel column chromatography (eluent: hexane/EtOAc = 10/1), followed by recrystallization from  $\text{CH}_2\text{Cl}_2$ /Hexane ( $v/v = 1/1$ ), to obtain the **1** in 19% (0.30 g, 0.69 mmol) as a green crystal.

#### 2,3,5,6-tetrafluoro-4-[(4-(diphenylaminophenyl)ethynyl]benzonitrile (**1**)



Yield: 19%; m.p.: 136.5 °C (**1-G**), 142.6 °C (**1-Y**) determined by DSC;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):

$\delta$  7.00 (d,  $J = 8.6$  Hz, 2H), 7.13–7.15 (m, 6H), 7.32 (t,  $J = 7.9$  Hz, 4H), 7.42 (d,  $J = 8.5$  Hz, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  73.5, 92.7, 107.7, 108.5, 111.9, 112.4, 120.9, 124.7, 125.9,

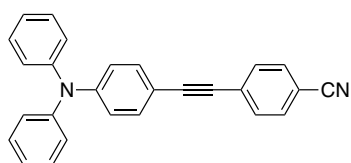
129.8, 133.5, 145.0–146.0 (dm,  $J = 76.5$  Hz), 146.7, 147.7–148.5 (dm,  $J = 70.6$  Hz),

150.2;  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  -133.61 (ddd,  $J = 24.3, 15.2, 6.2$  Hz), -134.59 (ddd,  $J = 24.4, 15.5, 6.4$  Hz); IR (KBr):  $\nu$  3033, 2239, 2197, 1645, 1583, 1518, 1491, 1338, 1302, 1266, 1181, 1072, 986, 929  $\text{cm}^{-1}$ ; HRMS (FAB+)  $m/z$  [ $\text{M}$ ]<sup>+</sup> calcd for  $\text{C}_{27}\text{H}_{14}\text{F}_4\text{N}_2$ : 442.1093; found: 442.1092.

### Typical synthesis procedure for 4-[2-[4-(diphenyl amino)phenyl]ethynyl]benzonitrile (1-H)

In a two-necked round-bottomed flask, equipped with a Teflon®-coated stirrer bar was placed 4-diphenylamino-phenyl acetylene (0.20 g, 0.76 mmol),  $\text{Cl}_2\text{Pd}(\text{PPh}_3)_2$  (0.024 g, 0.034 mmol),  $\text{PPh}_3$  (0.09 g, 0.034 mmol), 4-bromobenzonitrile (0.13 g, 0.69 mmol), and  $\text{Et}_3\text{N}$  (3 mL). To the resultant solution was added  $\text{CuI}$  (0.013 g, 0.069 mmol) and  $\text{Et}_3\text{N}$  (3 mL), and the whole was stirred at 80 °C overnight. After being stirred at the temperature for 22 h, precipitate formed in the reaction mixture was separated by atmospheric filtration and the filtrate was poured into saturated aqueous  $\text{NH}_4\text{Cl}$  solution (30 mL). Crude product was extracted with  $\text{EtOAc}$  (30 mL, three times) and organic layer combined was washed with brine (once). The collected organic layer was dried over anhydrous  $\text{Na}_2\text{SO}_4$ , which was separated by filtration. The filtrate was evaporated in vacuo and subjected to silica-gel column chromatography (eluent: hexane/ $\text{EtOAc}$  = 20/1), followed by recrystallization from  $\text{CH}_2\text{Cl}_2$ /Hexane (v/v = 1/1), to obtain the **1** in 73% (0.21 g, 0.55 mmol) as a white crystal.

### 4-[(4-diphenylaminophenyl)ethynyl]benzonitrile (1-H)



Yield: 73%; m.p.: 165.4-167.0 °C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.00 (d,  $J$  = 9.2 Hz, 2H), 7.06-7.13 (m, 6H), 7.28 (dd,  $J$  = 8.7 Hz, 6.5 Hz, 4H), 7.35 (d,  $J$  = 8.7 Hz, 2H), 7.55 (d,  $J$  = 8.4 Hz, 2H), 7.61 (d,  $J$  = 8.4 Hz, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  87.3, 94.7, 111.1, 114.6, 118.8, 121.9, 124.1, 125.4, 128.8, 130.0, 132.0, 132.1, 132.9, 147.1, 148.9; IR (KBr):  $\nu$  3040, 2939, 2214, 1913, 1685, 1624, 1598, 1540, 1519, 1479, 1450, 1433, 1405, 1318, 1105, 1003, 915  $\text{cm}^{-1}$ ; HRMS (FAB+)  $m/z$   $[\text{M}]^+$  calcd for  $\text{C}_{27}\text{H}_{18}\text{N}_2$ : 370.1470; found: 370.1465. The spectral data were fully in accordance with the reported data<sup>1</sup>.

## 2. NMR Spectra

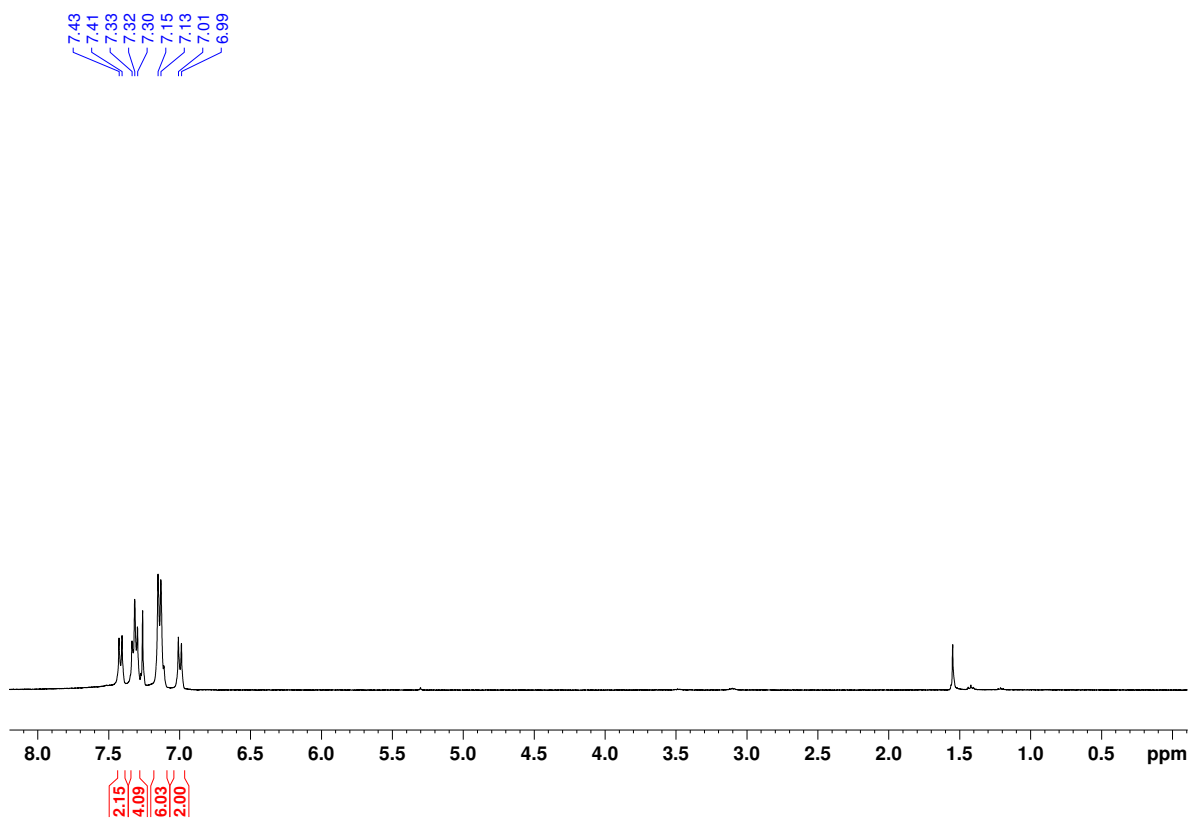


Figure S1.  $^1\text{H}$  NMR spectrum of **1** (400 MHz,  $\text{CDCl}_3$ )

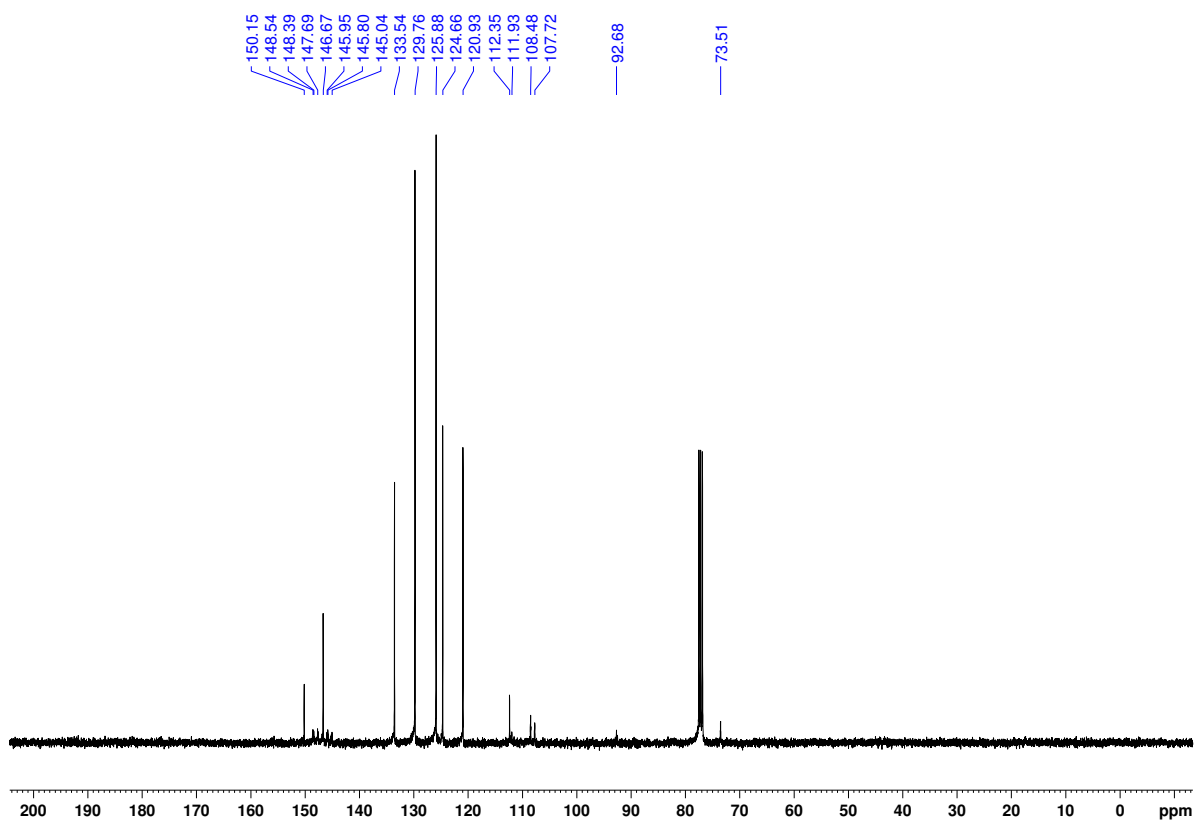
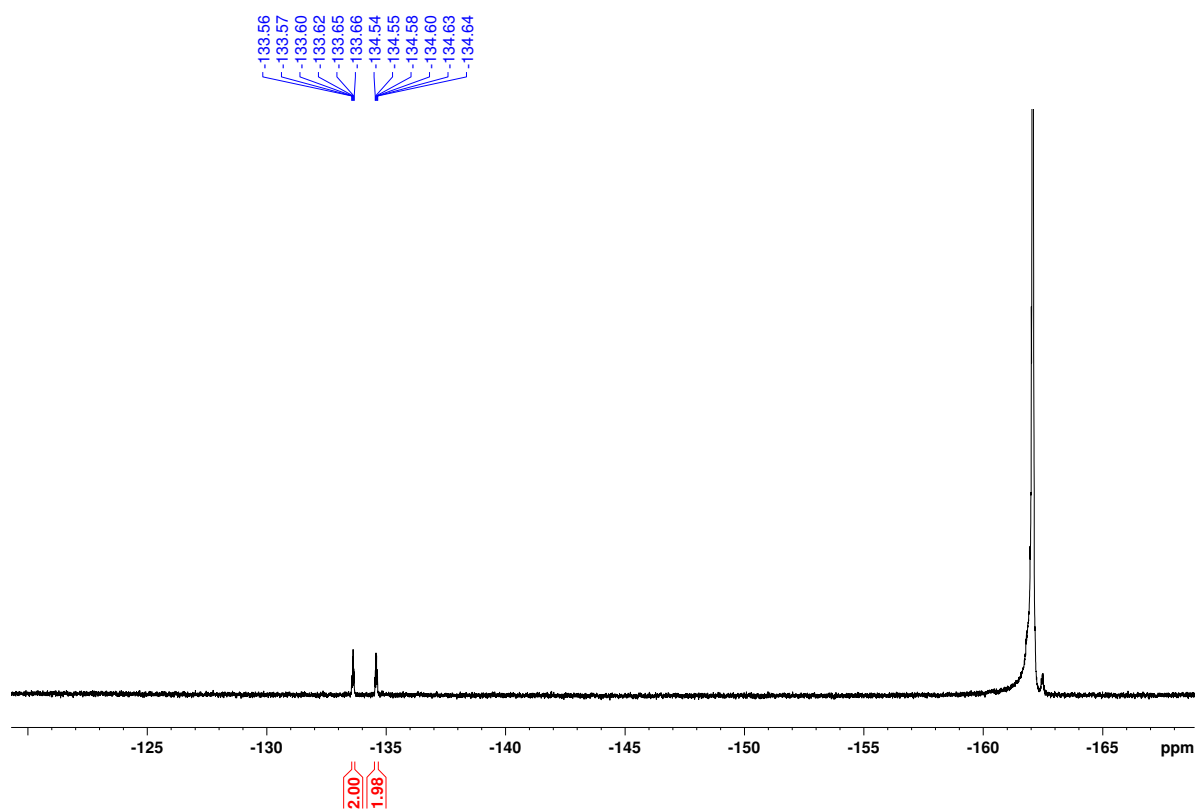


Figure S2.  $^{13}\text{C}$  NMR spectrum of **1** (100 MHz,  $\text{CDCl}_3$ )



**Figure S3.**  $^{19}\text{F}$  NMR spectrum of **1** (376 MHz,  $\text{CDCl}_3$ , hexafluoro benzene)

### 3. X-ray Crystallographic Analysis

XRD spectra were recorded on a Rigaku XtaLAB AFC11 diffractometer (Rigaku Corporation, Tokyo, Japan). The reflection data were integrated, scaled, and averaged using CrysAlisPro (ver. 1.171.39.43a, Rigaku Oxford Diffraction, 2015). Empirical absorption corrections were applied using the SCALE 3 ABSPACK scaling algorithm (CrysAlisPro). Structures were solved by a direct method (SHELXT-2018/2) and refined using a full-matrix least square method (SHELXL-2018/3) visualized by Olex2-1.3<sup>2,3</sup>.

**Table S1.** Crystallographic data of **1G**, **1Y**, **1-H**

	<b>1G</b>	<b>1Y</b>	<b>1-H</b>
CCDC #	2125133	2125132	2125131
Empirical Formula	C <sub>27</sub> H <sub>14</sub> F <sub>4</sub> N <sub>2</sub>	C <sub>27</sub> H <sub>14</sub> F <sub>4</sub> N <sub>2</sub>	C <sub>27</sub> H <sub>18</sub> N <sub>2</sub>
Formula weight	442.40	442.40	370.43
Temperature [K]	297	297	297
Crystal Color / Habit	Yellow / Plate	Orange / Needle	Colourless / block
Crystal Size [mm]	0.647 x 0.513 x 0.105	0.629 x 0.204 x 0.151	0.681 x 0.404 x 0.283
Crystal System	Triclinic	Monoclinic	Triclinic
Space Group	<i>P</i> -1	<i>P</i> 1 21/ <i>c</i> 1	<i>P</i> -1
<i>a</i> [Å]	9.8311(3)	7.1660(3)	7.6818(4)
<i>b</i> [Å]	10.2683(3)	21.8984(7)	9.1974(3)
<i>c</i> [Å]	22.2426(5)	13.6894(4)	15.4502(5)
<i>a</i> [°]	95.086(2)	90	76.568(3)
<i>b</i> [°]	100.768(2)	97.476(3)	78.786(4)
<i>g</i> [°]	95.042(2)	90	73.558(4)
<i>V</i> [Å <sup>3</sup> ]	2184.59(11)	2129.23(13)	1008.58(8)
<i>Z</i>	4	4	2
<i>R</i> [ <i>F</i> <sup>2</sup> > 2 <i>s</i> ( <i>F</i> <sup>2</sup> )] [a]	0.0459	0.0376	0.0409
<i>wR</i> <sub>2</sub> ( <i>F</i> <sup>2</sup> ) [b]	0.1363	0.1076	0.1201

[a]  $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ . [b]  $wR = \{[\sum w(|F_o| - |F_c|)] / \sum w|F_o|\}^{1/2}$ .

#### 4. DFT calculation

All computations were carried out using density functional theory (DFT) with the Gaussian 16 (Rev. B.01) package. Geometry optimizations were executed using the M06-2X hybrid functional and 6-31+G(d) basis set with a CPCM<sup>4</sup> for dichloromethane. Vertical excitations were also calculated using a TD-DFT method at the same level of theory.

**Table S2.** Dipole moment (debye) of **1**, **1-H** at franck-condon state.

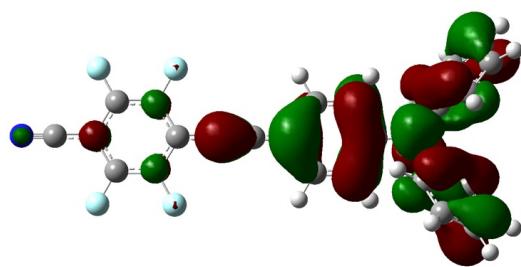
Dipole moment (debye)	
<b>1</b>	X= -10.0214/ Y= -0.0000/ Z= 0.0000/ Tot= 10.0214
<b>1-H</b>	X= 8.1848/ Y= 0.0000/ Z= 0.0000/ Tot= 8.1848

**Table S3.** Theoretical vertical transition behavior calculated by TD-DFT calculation.

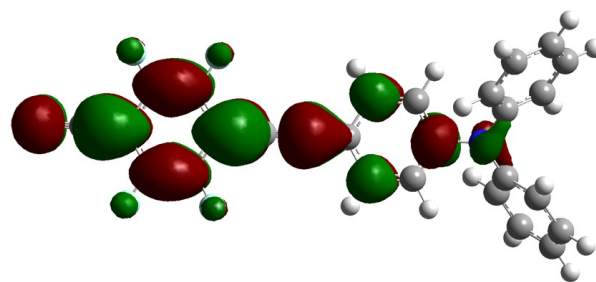
	Transition	Transition Energy (eV)	Theoretical Absorption (nm)	Oscillator strength / f
<b>1</b>	HOMO → LUMO	3.1963	387.90	1.4831
<b>1-H</b>	HOMO → LUMO	3.4505	359.32	1.4957

**Table S4.** Cartesian coordinate for **1** at the optimized geometry in S<sub>0</sub> state.

No.	Atom	Type	Coordinates (Angstroms)			24	7	0	9.555144	-0.000009	-0.000013
			X	Y	Z						
						25	7	0	-4.132638	-0.000001	0
1	6	0	4.869815	1.118877	-0.424841	26	6	0	-4.861411	-1.211906	-0.158303
2	6	0	6.252022	1.121026	-0.42542	27	6	0	-5.949389	-1.485145	0.676897
3	6	0	6.968804	-0.000002	-0.000004	28	6	0	-4.510754	-2.123501	-1.159826
4	6	0	6.25202	-1.121027	0.425416	29	6	0	-6.679617	-2.659407	0.507965
5	6	0	4.869813	-1.118872	0.424847	30	1	0	-6.220021	-0.772888	1.451497
6	6	0	4.141275	0.000005	0.000005	31	6	0	-5.234914	-3.303407	-1.311777
7	6	0	2.72376	0.000008	0.00001	32	1	0	-3.672115	-1.903054	-1.814635
8	6	0	1.509902	0.00001	0.000014	33	6	0	-6.323757	-3.575934	-0.482129
9	6	0	0.084838	0.000007	0.00001	34	1	0	-7.523678	-2.861822	1.160688
10	6	0	-0.631237	-1.123693	0.447365	35	1	0	-4.9541	-4.005205	-2.091561
11	6	0	-0.631239	1.123706	-0.447347	36	1	0	-6.890886	-4.493012	-0.607951
12	6	0	-2.016062	-1.12331	0.451993	37	6	0	-4.861416	1.211902	0.158299
13	1	0	-0.091216	-1.994922	0.805339	38	6	0	-4.510768	2.123498	1.159824
14	6	0	-2.016064	1.123317	-0.451983	39	6	0	-5.949391	1.485137	-0.676906
15	1	0	-0.09122	1.994936	-0.805319	40	6	0	-5.234932	3.303402	1.311771
16	6	0	-2.733661	0.000002	0.000003	41	1	0	-3.672131	1.903054	1.814637
17	1	0	-2.552652	-1.994438	0.813345	42	6	0	-6.679624	2.659396	-0.507978
18	1	0	-2.552656	1.994442	-0.813337	43	1	0	-6.220016	0.772879	-1.451508
19	9	0	6.904829	2.204355	-0.836219	44	6	0	-6.323772	3.575925	0.482118
20	9	0	4.223845	2.207844	-0.838381	45	1	0	-4.954125	4.005201	2.091557
21	9	0	4.22384	-2.207835	0.838392	46	1	0	-7.523683	2.861809	-1.160705
22	9	0	6.904824	-2.20436	0.836211	47	1	0	-6.890906	4.493001	0.607937
23	6	0	8.398395	-0.000006	-0.000009						



**HOMO**

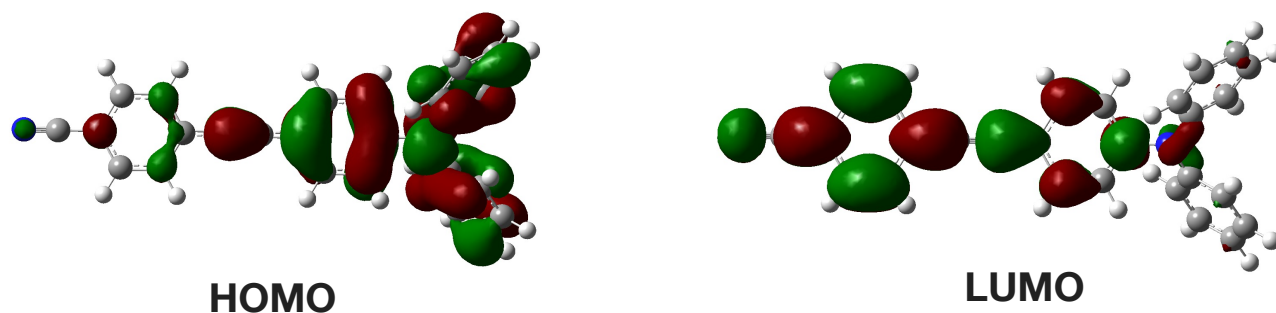


**LUMO**

**Table S5.** Cartesian coordinate for **1-H** at the optimized geometry in  $S_0$  state

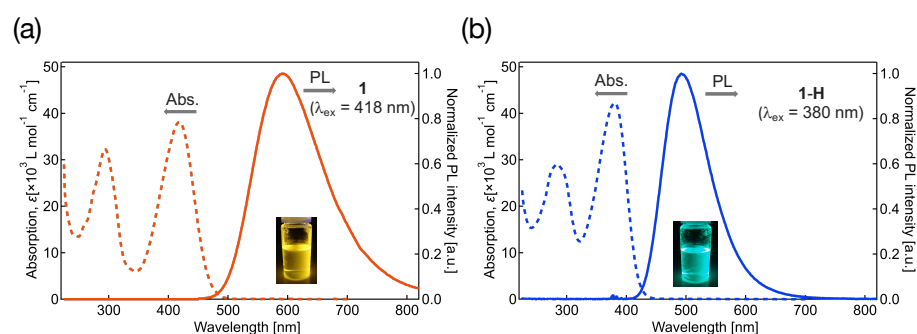
No.	Atom	Type	Coordinates (Angstroms)			24	6	0	-3.559415	-2.241479	0.92328
			X	Y	Z						
1	6	0	-1.106229	1.034439	0.626233	26	6	0	-4.270405	-3.438195	0.962235
2	6	0	0.280243	1.036102	0.62078	27	1	0	-2.700913	-2.090041	1.571767
3	6	0	0.997975	0	0	28	6	0	-5.776992	-2.606117	-0.724831
4	6	0	0.280242	-1.036103	-0.62078	29	1	0	-5.360482	-0.621735	-1.46343
5	6	0	-1.106229	-1.034439	-0.626233	30	6	0	-5.384103	-3.626292	0.142323
6	6	0	-1.821801	0	0	31	1	0	-3.959187	-4.22124	1.647471
7	1	0	-1.644842	1.836313	1.121452	32	1	0	-6.639804	-2.741316	-1.370469
8	1	0	0.819851	1.839393	1.113276	33	1	0	-5.940793	-4.557489	0.180191
9	1	0	0.81985	-1.839394	-1.113276	34	6	0	2.427384	-0.000001	-0.000001
10	1	0	-1.644842	-1.836313	-1.121452	35	6	0	3.641781	-0.000001	-0.000001
11	7	0	-3.226606	0	0	36	6	0	5.071684	0	0
12	6	0	-3.947316	1.223474	-0.044527	37	6	0	5.779737	-1.022641	-0.655281
13	6	0	-3.559414	2.241479	-0.92328	38	6	0	5.779737	1.022641	0.65528
14	6	0	-5.060435	1.412954	0.78199	39	6	0	7.166875	-1.024666	-0.65653
15	6	0	-4.270404	3.438195	-0.962235	40	1	0	5.233556	-1.811775	-1.161265
16	1	0	-2.700913	2.090041	-1.571767	41	6	0	7.166875	1.024666	0.65653
17	6	0	-5.776991	2.606117	0.724831	42	1	0	5.233555	1.811775	1.161264
18	1	0	-5.360482	0.621735	1.46343	43	6	0	7.861345	0	0
19	6	0	-5.384103	3.626292	-0.142323	44	1	0	7.714367	-1.813268	-1.162039
20	1	0	-3.959186	4.22124	-1.647471	45	1	0	7.714366	1.813269	1.162039
21	1	0	-6.639804	2.741317	1.370469	46	6	0	9.299986	0	0.000001
22	1	0	-5.940792	4.55749	-0.180191	47	7	0	10.458442	0.000001	0.000001
23	6	0	-3.947316	-1.223474	0.044527						



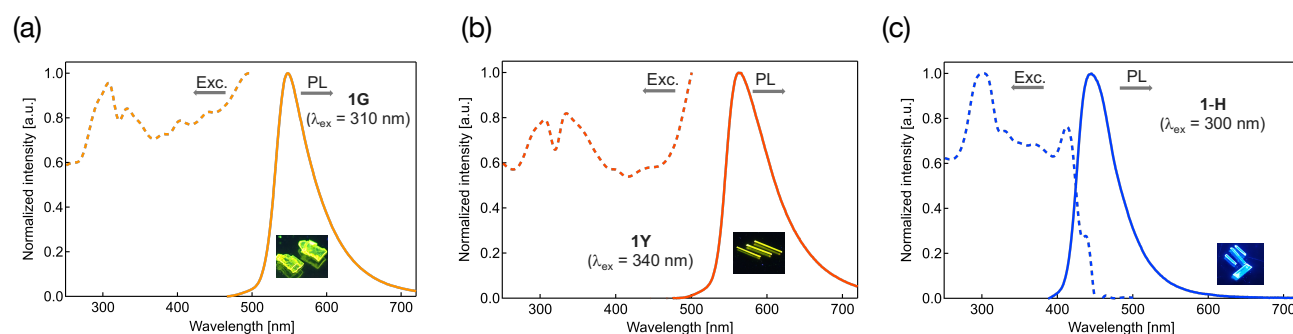


## 5. Photophysical Characteristics

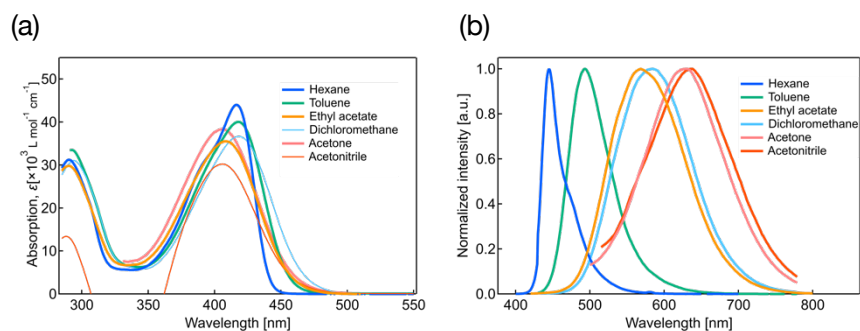
UV-vis absorption spectra were recorded on a JASCO V-500 absorption spectrometer. Steady-state PL spectra in solution and in crystal, and quantum yields were acquired using a JASCO FP-6600 fluorescence spectrometer or an absolute PL quantum yield measurement system (Quantaury-QY, Hamamatsu Photonics, C11347-01) with a calibrated integrating sphere.



**Figure S4.** UV-vis and PL spectra of **1**, **1-H** in  $\text{CH}_2\text{Cl}_2$  solution. Concentration:  $1.0 \times 10^{-5}$  mol  $\text{L}^{-1}$  for UV-vis and PL.



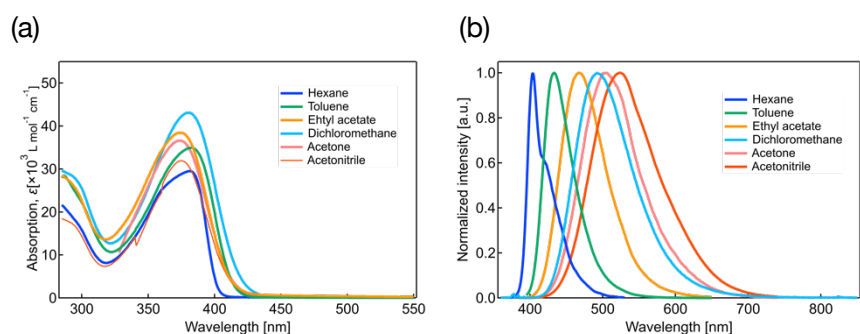
**Figure S5.** Excitation and PL spectra of **1G**, **1Y**, **1-H** in crystalline state. Excitation spectra were obtained by monitoring PL at the maximum PL wavelength ( $\lambda_{\text{em}} = 547$  nm for **1G**, 563 nm for **1Y**, 445 nm for **1-H**).



**Figure S6** (a) UV-vis and (b) PL spectra of **1** in different solvents (Excited with a light at the  $\lambda_{\text{abs}}$ ).

**Table S6.** Photophysical properties of **1** in different solvents.

	$\lambda_{\text{abs}}/\text{nm}$	$\lambda_{\text{em}}/\text{nm}$	$\Phi_{\text{em}}$
Hexane	417	445	1.00
Toluene	418	493	0.90
Ethyl acetate	409	568	0.41
Dichloromethane	412	585	0.45
Acetone	406	632	0.02
Acetonitrile	406	635	<0.01



**Figure S7** (a) UV-vis and (b) PL spectra of **1-H** in different solvents (Excited with a light at the  $\lambda_{\text{abs}}$ ).

**Table S7.** Photophysical properties of **1-H** in different solvents.

	$\lambda_{\text{abs}}/\text{nm}$	$\lambda_{\text{em}}/\text{nm}$	$\Phi_{\text{em}}$
Hexane	381	404, 420sh	0.56
Toluene	382	433	0.88
Ethyl acetate	374	467	0.87
Dichloromethane	380	491	0.97
Acetone	374	501	0.81
Acetonitrile	375	524	0.79

## 6. References

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