Supporting Information

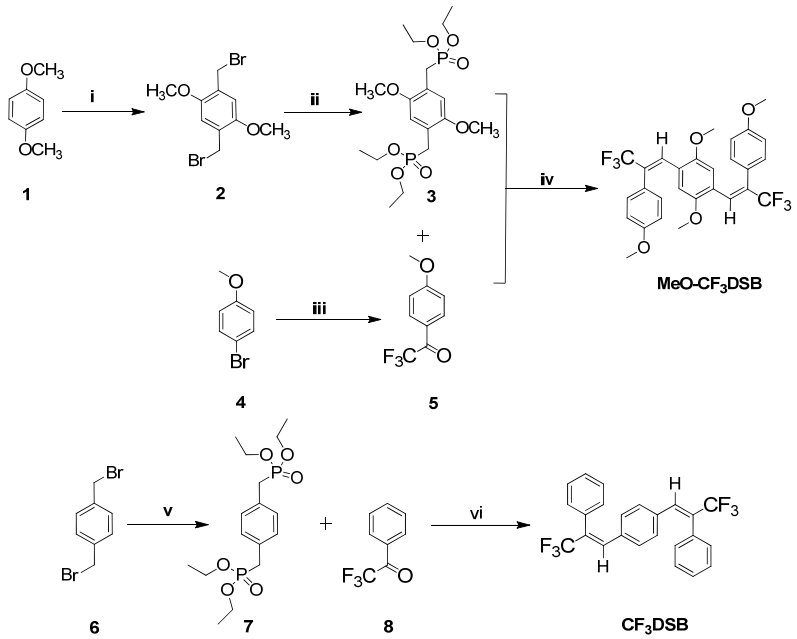
Aggregation Induced Emission (AIE) of Trifluoromethyl Substituted Distyrylbenzenes

Zhengwei Shi, [a] Joshua Davies, [a] Sei-Hum Jang, [a] Werner Kaminsky, [b] and Alex K.-Y. Jen*[ab]

[a] *Department of Materials Science and Engineering,* [b] *Department of Chemistry, University of Washington, Seattle, Washington 98195.*

E-mail: ajen@u.washington.edu

General. All reactions were carried out under an inert nitrogen atmosphere unless otherwise specified. Tetrahydrofuran (THF) was distilled over calcium hydride, and stored under nitrogen prior to use. All chemicals from Aldrich were used as received unless otherwise specified. All ^{1}H (500 MHz) and ^{13}C (125 MHz) spectra were recorded on Bruker AV500 spectrometers. Spectra were reported in parts per million from internal tetramethylsilane (δ 0.00 ppm) or residual protons of the deuterated solvent for ^{1}H NMR and from solvent carbon (e.g. δ 77.00 ppm for chloroform) for ^{13}C NMR. UV-Vis-NIR spectra were obtained on a Varian Cary 5000 spectrophotometer, while ESI-MS spectra were recorded on a Bruker Daltonics Esquire ion trap mass spectrometer. Melting temperatures (T_{mp}) were measured by differential scanning calorimetry (DSC) using a DSC2010 TA instruments with a heating rate of 10 ºC/min. Elemental analyses was performed by Intertek QTI Laboratory (Whitehouse, NJ).



Scheme S1. Synthetic route for **MeO-CF$_3$DSB** and **CF$_3$DSB**. (i) HBr/AcOH, AcOH, 80 °C, 3 h; (ii) triethylphosphite, 170 °C, 5 h; (iii) Mg/THF, ethyl trifluoroacetate/THF, - 78 °C, NH_4Cl aq. solution; (iv) potassium *tert*-butoxide/THF, aq. solution, room temperature, 10 h; (v) triethylphosphite, 170 °C, 5 h; (vi) potassium *tert*-butoxide/THF, aq. solution, room temperature, 10 h.

Synthesis of 2,5-bis(bromomethyl)-1,4-dimethoxybenzene (2) from 1,4-dimethoxybenzene (1)

27 mL of 33% HBr/acetic acid solution was added to the suspension of 1,4-dimethoxybenzene **1** (4.1 g, 30 mmol) and paraformaldehyde (2.0 g, 66 mmol) in acetic acid (100 mL) at 80 °C. The resultant clear solution was stirred for another 3 h, cooled, and crystallized for 20 h at 4 °C. The sold precipitate was filtered, washed with water, and dried in vacuum to afford the compound **2** as white solid (7.34 g, 22.8 mmol, 76%). ^{1}H NMR ($CDCl_3$): δ 6.87 (s, 2 H), 4.53 (s, 4 H), 3.87 (s, 6 H); ^{13}C NMR ($CDCl_3$): δ 28.79, 56.48, 114.08, 127.66, 151.51.

Synthesis of 2,5-bis(diethoxyphosphorylmethylene)-1,4-dimethoxybenzene (3) from 1,4-bis(bromomethyl)-2,5-dimethoxybenzene (2)

The mixture of compound **2** (6.44 g, 20 mmol) and triethylphosphite (50 mL) was heated to reflux for 5 h. Afterwards, unreacted triethylphosphite was removed under the reduced pressure. The remaining white slurry was poured into a large amount of hexanes to extract residual triethylphosphite. The compound **3** was obtained through filtration as white solid (7.62 g, 17.4 mmol, 87%). ^{1}H NMR ($CDCl_3$): δ 6.93 (s, 2H), 4.05 (t, *J*=7.5 Hz, 8H), 3.81 (s, 6H), 3.26 (d, *J*=20 Hz, 4H), 1.27 (t, *J*=7.0 Hz, 12H). ^{13}C NMR ($CDCl_3$): δ 151.0, 119.5, 114.1, 61.9, 56.1, 27.0, 25.9, 16.3.

Synthesis of 4'-methoxy-2,2,2-trifluoroacetophenone (5) from 4-methoxyphenyl magnesium bromide (4)

To a solution of ethyl trifluoroacetate (4.26 g, 30 mmol) in THF at –78 °C (50 mL) was added a THF solution of 4-methoxyphenyl magnesium bromide (prepared from 4-bromoanisole (3.72 g, 20 mmol) dropwise and Mg (0.51 g, 21 mmol); 15 mmol). After stirring at the reaction mixture for another 1 h at –78 °C, the reaction was quenched with sat. NH_4Cl aq., followed by an addition of 2 M HCl aq., and the mixture was extracted with ethyl acetate three times. The combined organic layers was washed with brine, dried over anhydrous Na_2SO_4, concentrated in vacuo. The oily residue was purified by silica gel column chromatography and distilled to give compound **5** (2.46 g, 12 mmol, 80 %). ^{1}H NMR ($CDCl_3$): δ 8.07 (m, 2H), 7.01 (m, 2H), 3.91 (s, 3H); ^{13}C NMR ($CDCl_3$): δ 178.9, 156.4, 132.7, 122.8, 116.9, 114.4, 55.7.

Synthesis of 1,4-bis(diethylphosphono)dimethylbenzene (7) from 1,4-bis(bromomethyl)benzene (6)

The mixture of 1,4-bis(bromomethyl)benzene **6** (1.3 g, 4.93 mmol) and triethylphosphite (20 mL) was heated to reflux for 5 h. Afterwards, access triethylphosphite was removed under the reduced pressure. The remaining white slurry was poured into a large amount of hexanes to extract residual remains of triethylphosphite. A white solid of compound **7** was obtained by filtration (1.79 g, 4.73 mmol, 96%). ^{1}H NMR ($CDCl_3$): δ 7.24 (s, 4H), 4.01 (t, *J*=7.5 Hz, 8H), 3.16 (d, *J*=20 Hz, 4H), 1.23 (t, *J*=7.0 Hz, 12H).

Synthesis of MeO-CF_3DSB

The solution of compound **3** (0.88 g, 2.0 mmol), and compound **5** (0.90 g, 4.4 mmol) in THF (15 mL) was stirred at room temperature overnight after the slow addition of potassium *tert*-butoxide (1 M in THF, 4.2 mL, 4.2 mmol) under nitrogen atmosphere. The reaction was quenched with sat. NH_4Cl aq. and was extracted with 20 ml of ethyl acetate three times. The combined organic layers was washed with brine, dried over anhydrous Na_2SO_4, concentrated in vacuo. The residue was purified by silica gel column chromatography to give **MeO-CF_3DSB** as yellowish crystals (0.85 g, 1.58 mmol, 79 %). ^{1}H NMR ($CDCl_3$): δ 7.39 (d, *J*=1.5 Hz, 2H), 7.20 (d, *J*=8.5 Hz, 4H), 6.91 (d, *J*=8.0 Hz, 4H), 6.25 (s, 2H), 3.80 (s, 6H), 3.24 (s, 6H). ^{13}C NMR ($CDCl_3$): δ 159.91, 151.25, 131.23, 130.10 (q, ^{13}C - ^{19}F *J*= 115 Hz), 127.03 (q, ^{13}C - ^{19}F *J*= 20 Hz), 125.16, 124.99, 123.62, 122.81, 114.44,

112.37, 55.36. ^{19}F NMR ($CDCl_3$): δ -64.75 (d, ^{1}H - ^{19}F *J*= 1.5 Hz). HRMS (ESI) (M^+, $C_{28}H_{24}F_6O_4$): Calcd: 538.1579; Found: 538.1566. *Anal. Calcd* for $C_{28}H_{24}F_6O_4$: C, 62.45; H, 4.49. *Found: C, 62.41; H, 3.89.*

Synthesis of CF_3DSB

The solution of compound **7** (0.76 g, 2.0 mmol), and 2,2,2-trifluoroacetophenone (0.76 g, 4.4 mmol) in THF (10 mL) was stirred at room temperature overnight after the slow addition of potassium *tert*-butoxide (1 M in THF, 4.2 mL, 4.2 mmol) under nitrogen atmosphere. The reaction was quenched with sat. NH_4Cl aq. and was extracted with ethyl acetate three times. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, concentrated in vacuo. The residue was purified by silica gel column chromatography to give **CF_3DSB** as a white crystal (0.73 g, 1.74 mmol, 85 %). ^{1}H NMR ($CDCl_3$): δ 7.37 - 7.32 (overlap, 6H), 7.22 (d, *J*=6.0 Hz, 4H), 7.08 (d, *J*=1.5 Hz, 2H), 6.77 (s, 4H). ^{13}C NMR ($CDCl_3$): δ 134.21, 132.59, 132.48 (q, ^{13}C - ^{19}F *J* = 18 Hz), 131.46 (q, ^{13}C - ^{19}F *J*= 89 Hz),130.06, 129.91, 129.17, 129,12, 124.89, 122.72. ^{19}F NMR ($CDCl_3$): δ -66.81 (d, ^{1}H - ^{19}F *J* = 1.5 Hz). HRMS (ESI) (M^+, $C_{24}H_{16}F_6$): Calcd: 418.1156; Found: 441.1043 ($[M+Na]^+$). *Anal. Calcd* for $C_{24}H_{16}F_6$: C, 68.90; H, 3.85. *Found:* C, 68.88; H, 3.64.

Quantum mechanical calculations:

All DFT[S1,S2] calculations were performed using Gaussian 09(A.02)[S3] employing the hybrid B3LYP[S4,S5] exchange-correlation functional with a split valence 6-31G* [S6] basis set. This computational method is found to be an accurate formalism for predicting the geometric and electronic properties of many conjugated organic molecules.[S7] In addition, frequency calculations were performed on the optimized geometries and minima were verified through normal mode analyses to check for imaginary modes. It is worth mentioning that the DFT, and crystal structures had nearly superimposable geometries.

Fig. S1 HOMO (left), LUMO (right) surfaces and energy level (ev) for **MeO-CF_3DSB** and **CF_3DSB**. All calculations were performed using Gaussian09(A.02)[S3] employing the B3LYP[S4,S5] functional with a 6-31G* [S6] basis set.

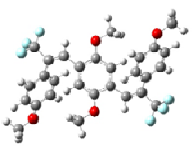
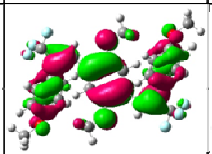
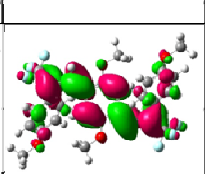
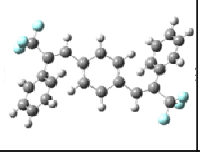
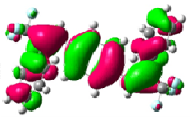
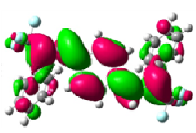
Entity	Geometry	HOMO	LUMO	Energy Level		
				HOMO	LUMO	ΔE
MeO-CF_3DSB				-5.36	-1.77	3.59
CF_3DSB				-6.10	-1.99	4.11

Fig. S2 Natural population analysis (NPA) charge for **MeO-CF$_3$DSB** and **CF$_3$DSB** from NBO calculation.

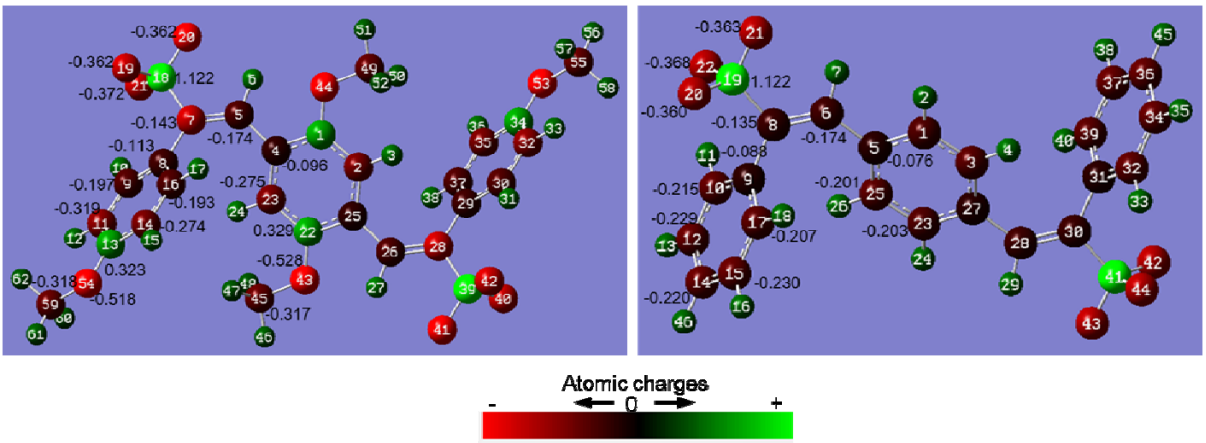


Fig. S3 PL spectra of **MeO-CF$_3$DSB** (a) and **CF$_3$DSB** (b) in THF/water mixtures with different water fractions (fw). Concentration: 10 μM; excitation wavelength: **MeO-CF$_3$DSB**, 380 nm; **CF$_3$DSB**, 310 nm.

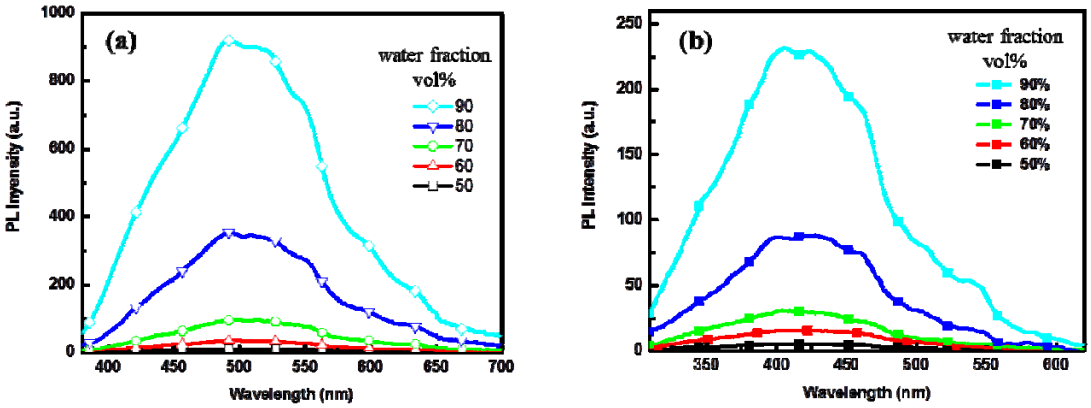
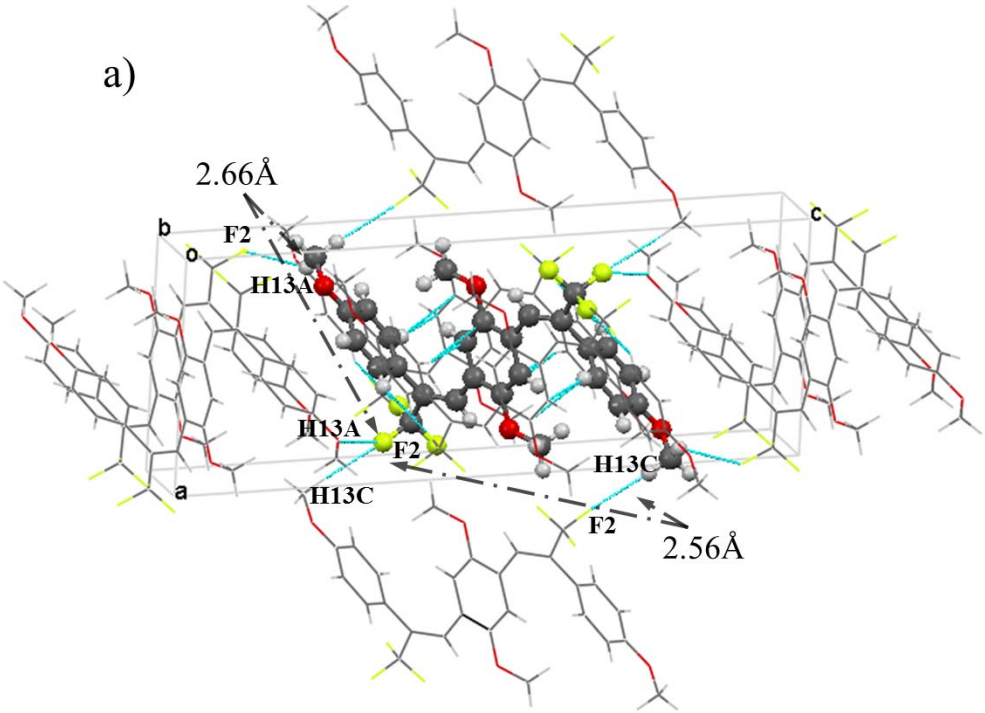


Fig. S4 Crystal structure, short contact and molecular packing models in **MeO-CF$_3$DSB** single crystal. (a) viewed down the *b* axis. (b) viewed down the *a* axis. Notes: Along the *b* axis, C13–H13A… F2–C12 (at 1-x, -1/2+y, -1/2-z) contact distance is 2.66 Å to form a networked contact between the protons of terminal methoxy group and the fluorine atoms in CF_3 in two adjacent molecules (Fig. S4a). In addition, along the *a* axis, C12–F2…H13C–C13 (at -1+x, y, z) contact distance is 2.56 Å to form a networked contact between the protons of terminal methoxy group and the fluorine atoms in CF_3 in two adjacent molecules (Fig. S4a). The network consists primarily of C12–F3…H11–C11 (at x,-1+y, z) interactions between the fluorine atom and the terminal phenyl aromatic proton (2.64 Å), and aromatic C7–H7…π (at x,-1+y, z) interactions between the terminal phenyl aromatic proton and the central phenyl ring (2.89 Å) (Fig. S4b). In addition, the distance of two adjacent molecules along the *b* axis is identical to the unit *b* axis length (5.79 Å) (Fig. S4b). The symmetry operation details are as following:

Number	Symmetry Operation	Description	Detailed Description
1	x, y, z	Identity	Identity
2	-x, 1/2+y, 1/2-z	Screw axis (2-fold)	2-fold screw axis with direction [0, 1, 0] at 0, y, 1/4, with screw component [0, 1/2, 0]
3	-x, -y, -z	Inversion centre	Inversion at [0, 0, 0]
4	x, 1/2-y, 1/2+z	Glide plane	Glide plane perpendicular to [0, 1, 0] with glide component [0, 0, 1/2]



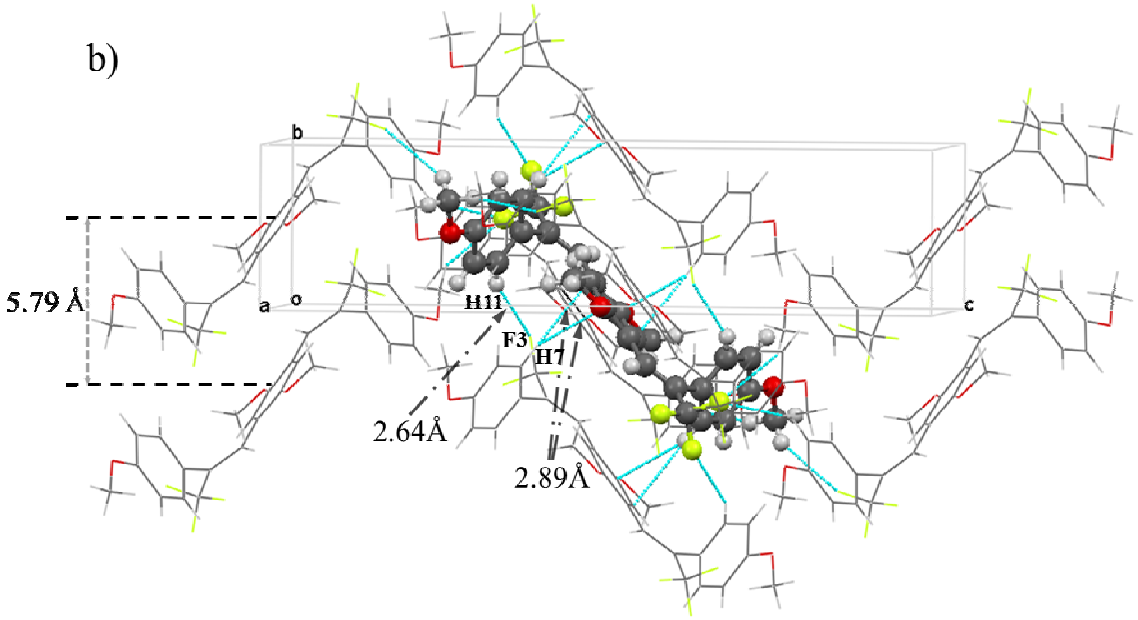
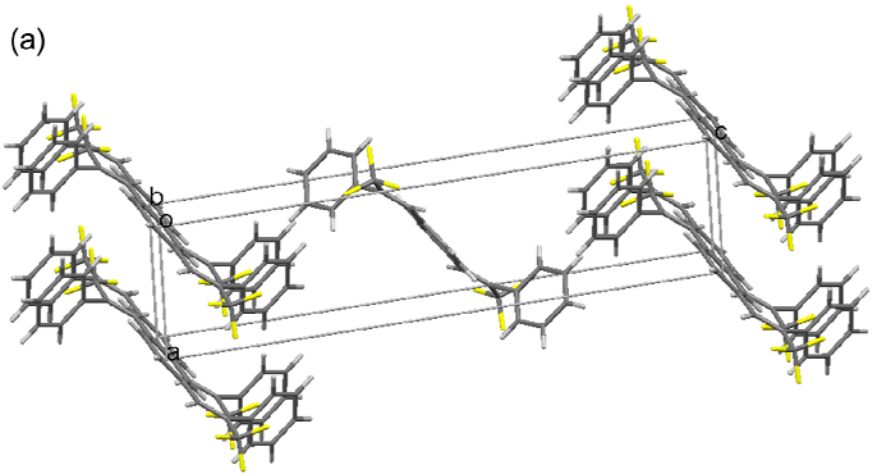


Fig. S5 **CF_3DSB** single crystal (a) unit packing diagram viewed down the *b* axis, (b) crystal structure, short contact and molecular packing models viewed down the *a* axis. Notes: C4-H4…F4 (at 1-x, 1-y, -z) distance is 2.57 Å, and C11-H11 …C1 and C3 (at 1+x, y, z) distances are 2.85 Å (Fig. S5b). The symmetry operation details are as following:

Number	**Symmetry Operation**	**Description**	**Detailed Description**
1	x, y, z	Identity	Identity
2	1/2-x, 1/2+y, 1/2-z	Screw axis (2-fold)	2-fold screw axis with direction [0, 1, 0] at 1/4, y, 1/4 with screw component [0, 1/2, 0]
3	-x, -y, -z	Inversion centre	Inversion at [0, 0, 0]
4	1/2+x, 1/2-y, 1/2+z	Glide plane	Glide plane perpendicular to [0, 1, 0] with glide component [1/2, 0, 1/2]



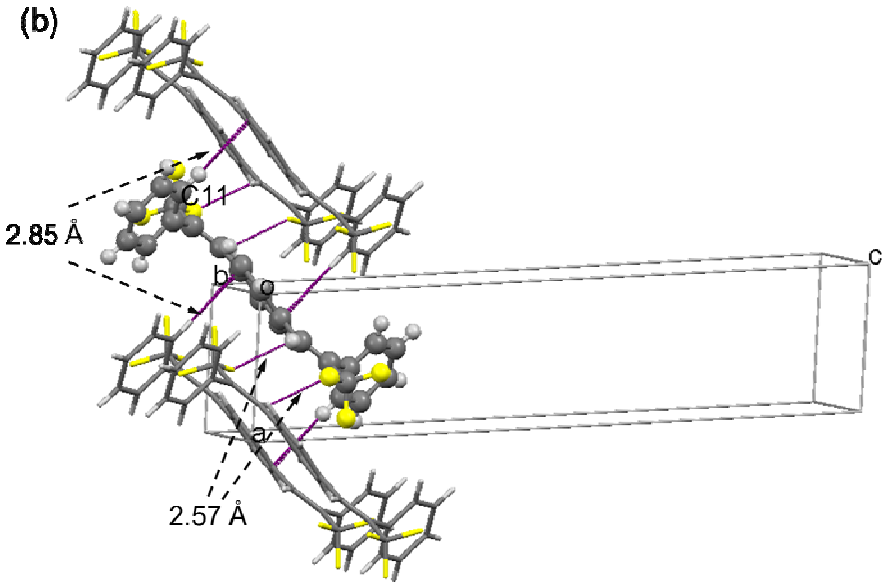


Fig. S6 DSC thermal analysis of **MeO-CF$_3$DSB** and **CF$_3$DSB** at 10 °C/min under nitrogen.

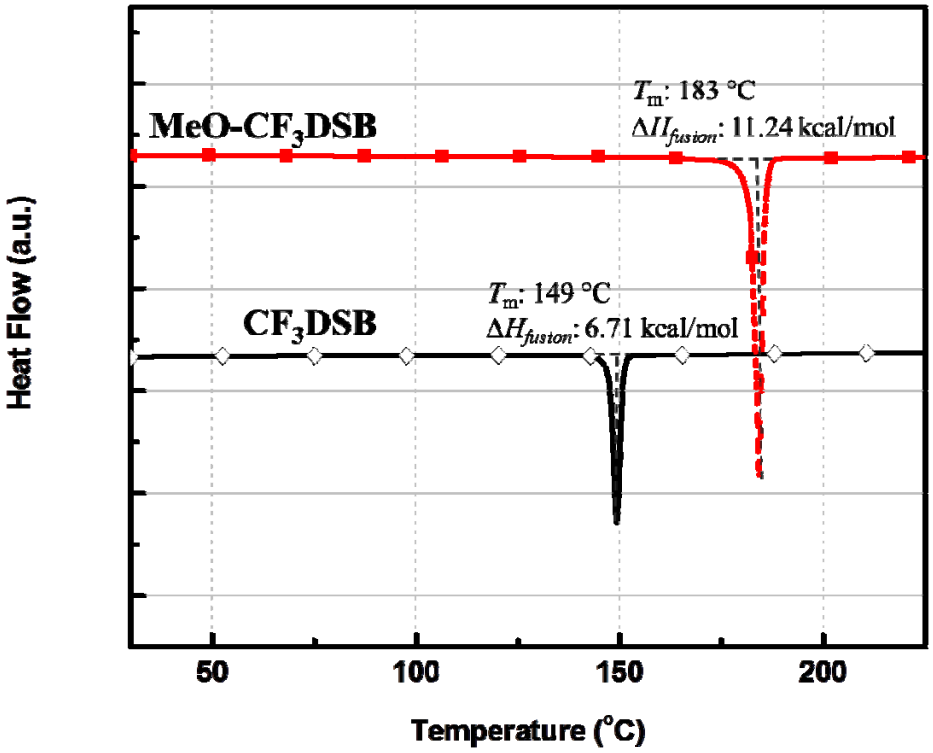


Fig. S7 High resolution Mass Spectra of **MeO-CF$_3$DSB** (top) and **CF$_3$DSB** (bottom).

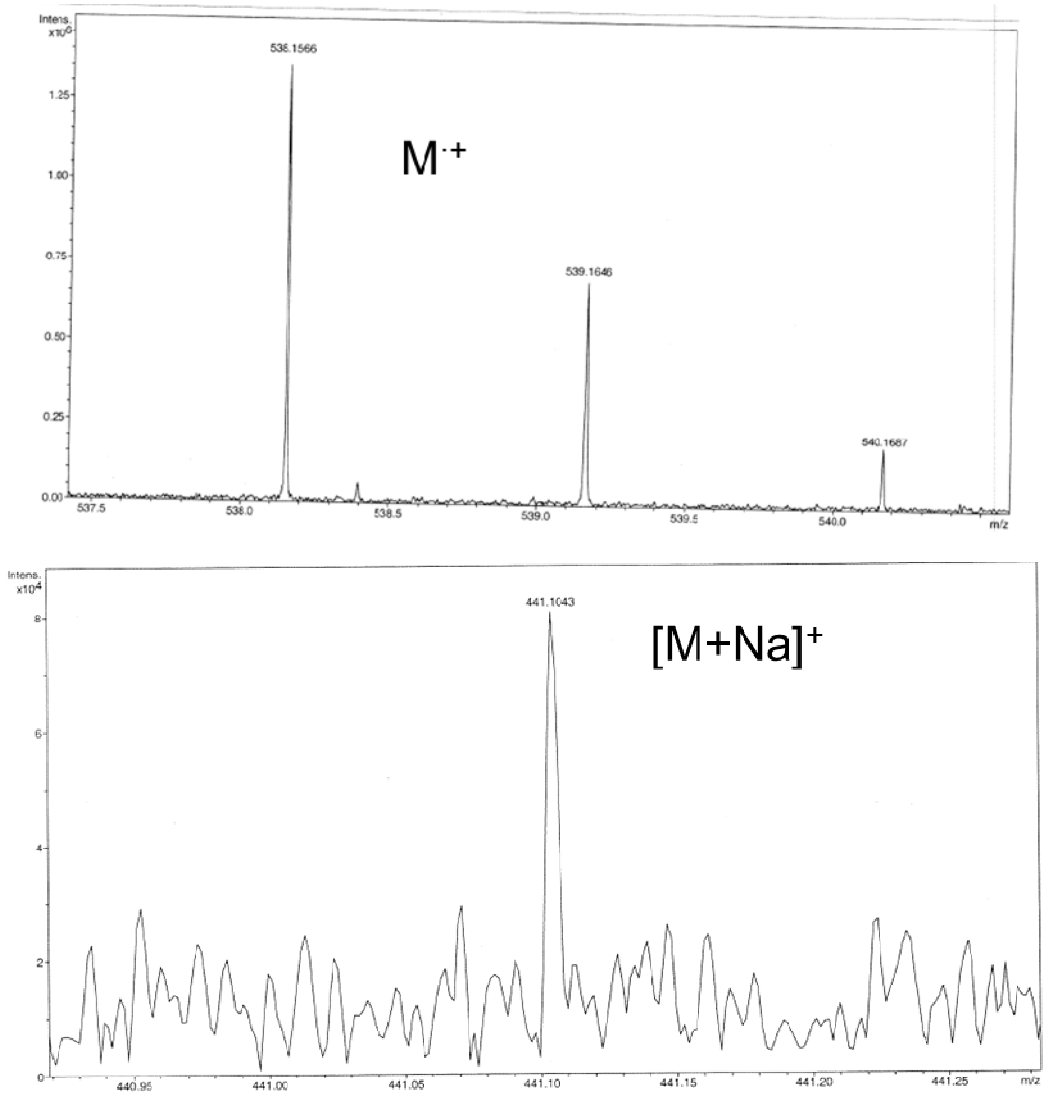


Table S1. Crystal Data and Structure Refinements of **MeO-CF$_3$DSB** and **CF$_3$DSB.** Notes: the digits in the parentheses indicate the error margin.

identification code	**MeO-CF$_3$DSB**	**CF$_3$DSB**
empirical formula	C28H24F6O4	C24H16F6
formula weight	538.47	418.37
temperature/K	100(2)	110(2)
crystal system	Monoclinic	Monoclinic
space group	P 2_1/c	P 2_1/n
a/Å	8.8528(6)	5.4710(6)
b/Å	5.7949(4)	7.640(2)
c/Å	23.443(17)	23.076(7)
α/°	90.00	90.00
β/°	94.862(3)	95.405(14)
γ/°	90.00	90.00
V/ Å^3	1198.32(14)	960.3(5)
Z	2	2
Density/Mg/m^3	1.492	1.447
Absorption coefficient	0.130	0.124
F(000)	556	428
θ range/°	1.74 to 28.45	1.77 to 28.32
index range	-11 ≤ h ≥ 11, -7 ≤ h ≥ 7, -31 ≤ h ≥ 31,	-7<=h<=7, -10<=k<=10, -30<=l<=30
reflections collected	54014	7011
independent reflections	2983 [R(int) = 0.0208]	2390 [R(int) = 0.0364]
completeness to θ = 25.00°	98.9%	99.8%
data/restraints/params	2983 / 0 / 174	2390 / 0 / 136
good-of-fit on F^2	1.032	1.012
final R indices [I>2σ(I)]	R1 = 0.0305, wR2 = 0.0760	R1 = 0.0518, wR2 = 0.1090
R indices (all data)	R1 = 0.0344, wR2 = 0.0800	R1 = 0.0830, wR2 = 0.1209
largest diff. peak and hole / e·Å^{-3}	0.420 and -0.267	0.272 and -0.268

Table S2. Optimized coordinates of **MeO-CF$_3$DSB** from DFT calculations

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.192577	1.271560	-0.553102
2	6	0	-1.230694	0.342993	-0.548102
3	1	0	-2.183543	0.592345	-0.993585
4	6	0	1.070114	0.937437	-0.005698
5	6	0	2.113660	1.966801	0.034561
6	1	0	1.727912	2.980357	0.043967
7	6	0	3.457110	1.828023	0.069403
8	6	0	4.231758	0.570223	-0.113376
9	6	0	5.238552	0.175193	0.777803
10	1	0	5.462491	0.791936	1.641042
11	6	0	5.966807	-1.001230	0.583426
12	1	0	6.734939	-1.270750	1.299338
13	6	0	5.700000	-1.808141	-0.527943
14	6	0	4.701802	-1.421242	-1.436949
15	1	0	4.517773	-2.048210	-2.303840
16	6	0	3.986800	-0.251393	-1.231212
17	1	0	3.225312	0.041394	-1.947323
18	6	0	4.288216	3.078197	0.245576
19	9	0	5.259615	3.168622	-0.689684
20	9	0	3.568160	4.218282	0.181311
21	9	0	4.917354	3.091460	1.455445
22	6	0	0.192588	-1.271546	0.553110
23	6	0	1.230706	-0.342980	0.548110
24	1	0	2.183555	-0.592332	0.993592
25	6	0	-1.070103	-0.937423	0.005706
26	6	0	-2.113646	-1.966789	-0.034554
27	1	0	-1.727894	-2.980343	-0.043967
28	6	0	-3.457097	-1.828017	-0.069394
29	6	0	-4.231753	-0.570224	0.113385
30	6	0	-5.238540	-0.175200	-0.777803
31	1	0	-5.462463	-0.791943	-1.641047
32	6	0	-5.966811	1.001214	-0.583429
33	1	0	-6.734936	1.270730	-1.299349
34	6	0	-5.700026	1.808120	0.527948
35	6	0	-4.701838	1.421225	1.436966
36	1	0	-4.517827	2.048189	2.303865

37	6	0	-3.986820	0.251385	1.231231
38	1	0	-3.225340	-0.041399	1.947352
39	6	0	-4.288199	-3.078188	-0.245591
40	9	0	-5.259590	-3.168637	0.689675
41	9	0	-3.568141	-4.218274	-0.181363
42	9	0	-4.917350	-3.091417	-1.455454
43	8	0	0.301618	-2.526512	1.085360
44	8	0	-0.301606	2.526527	-1.085351
45	6	0	1.572455	-2.955075	1.553042
46	1	0	1.442087	-3.996322	1.853287
47	1	0	2.334159	-2.891213	0.765746
48	1	0	1.899664	-2.367309	2.420616
49	6	0	-1.572442	2.955092	-1.553031
50	1	0	-2.334146	2.891231	-0.765734
51	1	0	-1.442073	3.996340	-1.853275
52	1	0	-1.899653	2.367329	-2.420606
53	8	0	-6.347418	2.971989	0.819031
54	8	0	6.347374	-2.972018	-0.819025
55	6	0	-7.392286	3.394545	-0.043865
56	1	0	-7.772542	4.325325	0.380598
57	1	0	-7.024549	3.583980	-1.061053
58	1	0	-8.203387	2.656030	-0.085633
59	6	0	7.392249	-3.394581	0.043859
60	1	0	7.024524	-3.584004	1.061053
61	1	0	7.772488	-4.325370	-0.380603
62	1	0	8.203359	-2.656076	0.085610

Table S3. Optimized coordinates of **CF_3DSB** from DFT calculations

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.162000	-1.246967	-0.577315
2	1	0	-0.283924	-2.225067	-1.036587
3	6	0	1.099374	-0.667314	-0.545321
4	1	0	1.937175	-1.191690	-0.988828
5	6	0	-1.291958	-0.595674	-0.044743
6	6	0	-2.579828	-1.300573	-0.099667
7	1	0	-2.482956	-2.378840	-0.198487
8	6	0	-3.838265	-0.818894	-0.045193
9	6	0	-4.247752	0.615108	-0.050526
10	6	0	-4.999739	1.168659	0.997962
11	1	0	-5.282748	0.547516	1.840945
12	6	0	-5.380566	2.510604	0.962947
13	1	0	-5.956722	2.925943	1.785398
14	6	0	-5.027332	3.314996	-0.121427
15	6	0	-4.290196	2.770007	-1.175008
16	1	0	-4.018610	3.386441	-2.027740
17	6	0	-3.904914	1.431159	-1.140833
18	1	0	-3.336066	1.006888	-1.962937
19	6	0	-4.982723	-1.806454	-0.038006
20	9	0	-5.890584	-1.516476	-0.995184
21	9	0	-4.591460	-3.084173	-0.233957
22	9	0	-5.647658	-1.783119	1.148140
23	6	0	0.161958	1.246895	0.577301
24	1	0	0.283880	2.224997	1.036569
25	6	0	-1.099416	0.667242	0.545307
26	1	0	-1.937222	1.191621	0.988804
27	6	0	1.291918	0.595601	0.044733
28	6	0	2.579780	1.300517	0.099656
29	1	0	2.482886	2.378781	0.198477
30	6	0	3.838232	0.818876	0.045182
31	6	0	4.247782	-0.615110	0.050536
32	6	0	4.999704	-1.168666	-0.997995
33	1	0	5.282612	-0.547542	-1.841026
34	6	0	5.380594	-2.510593	-0.962963
35	1	0	5.956696	-2.925938	-1.785447
36	6	0	5.027490	-3.314959	0.121473
37	6	0	4.290424	-2.769962	1.175100
38	1	0	4.018943	-3.386375	2.027880
39	6	0	3.905079	-1.431133	1.140906
40	1	0	3.336285	-1.006855	1.963044
41	6	0	4.982654	1.806477	0.037983
42	9	0	5.890506	1.516564	0.995190

43	9	0	4.591336	3.084187	0.233887
44	9	0	5.647613	1.783130	-1.148148
45	1	0	5.328361	-4.358768	0.148073
46	1	0	-5.328154	4.358819	-0.148012

Table S4. Bond lengths [Å] for **MeO-CF_3DSB** and **CF_3DSB from X-Ray analysis.** Notes: the digits in the parentheses indicate the error margin.

MeO-CF_3DSB			**CF_3DSB** [S8]	
Bond	Bond lengths [Å]		Bond	Bond lengths [Å]
C(1)-C(2)	1.3888(13)		C(1)-C(2)#1	1.380(3)
C(1)-C(3)	1.4024(13)		C(1)-C(3)	1.397(3)
C(1)-H(1)	0.9500		C(1)-H(1A)	0.9500
C(2)-O(1)	1.3667(11)		C(2)-C(1)#1	1.380(3)
C(2)-C(3)#1	1.4116(13)		C(2)-C(3)	1.397(3)
C(3)-C(2)#1	1.4116(13)		C(2)-H(2)	0.9500
C(3)-C(4)	1.4683(13)		C(3)-C(4)	1.465(3)
C(4)-C(5)	1.3445(13)		C(4)-C(5)	1.332(3)
C(4)-H(4)	0.9500		C(4)-H(4)	0.9500
C(5)-C(6)	1.4918(13)		C(5)-C(6)	1.494(3)
C(5)-C(12)	1.5039(13)		C(5)-C(12)	1.499(3)
C(6)-C(7)	1.3932(13)		C(6)-C(7)	1.388(3)
C(6)-C(11)	1.4030(13)		C(6)-C(11)	1.388(3)
C(7)-C(8)	1.3943(13)		C(7)-C(8)	1.383(3)
C(7)-H(7)	0.9500		C(7)-H(7)	0.9500
C(8)-C(9)	1.3948(14)		C(8)-C(9)	1.379(3)
C(8)-H(8)	0.9500		C(8)-H(8)	0.9500
C(9)-O(2)	1.3668(11)		C(9)-C(10)	1.382(3)
C(9)-C(10)	1.3976(14)		C(9)-H(9)	0.9500
C(10)-C(11)	1.3886(13)		C(10)-C(11)	1.387(3)
C(10)-H(10)	0.9500		C(10)-H(10)	0.9500
C(11)-H(11)	0.9500		C(11)-H(11)	0.9500
C(12)-F(1)	1.3396(11)		C(12)-F(2)	1.336(2)
C(12)-F(3)	1.3465(11)		C(12)-F(3)	1.339(3)
C(12)-F(2)	1.3528(11)		C(12)-F(1)	1.338(2)
C(13)-O(2)	1.4282(13)			
C(13)-H(13A)	0.9800			
C(13)-H(13B)	0.9800			
C(13)-H(13C)	0.9800			
C(14)-O(1)	1.4226(12)			

C(14)-H(14A)	0.9800			
C(14)-H(14B)	0.9800			
C(14)-H(14C)	0.9800			

References

S1. P. Hohenberg, W. Kohn, *Phys. Rev.* 1964, **136**, B864.

S2. W. Kohn, L. J. Sham, *Phys. Rev.* 1965, **140**, A1133.

S3. Gaussian 09, Revision A.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A.F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, Jr. J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, N. J. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

S4. C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B: Condens. Matter* 1988, **37**, 785.

S5. A. D. Becke, *J. Chem. Phys.* 1993, **98**, 5648.

S6. R. Ditchfield, W. J. Hehre, J. A. Pople, *J. Chem. Phys.* 1971, **54**, 724.

S7. N. Blouin, A. Michaud, D. Gendron, S. Wakim, E. Blair, R. Neagu-Plesu, M, Belletête, G, Durocher, Y. Tao, and M. Leclerc, *J. Am. Chem. Soc.* 2008, **130**, 732.