Effect of Substitution on Second-order Nonlinear Optical Properties in Ferrocene Appended Donor-π-Acceptor Y-shaped Trifluoromethyl Imidazole Chromophores

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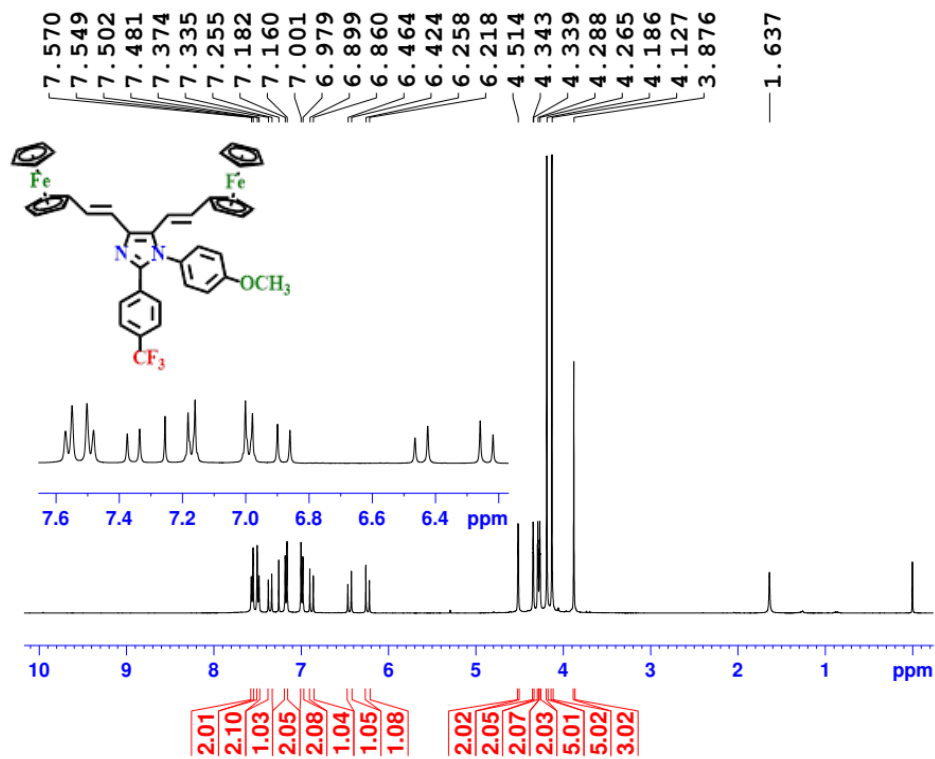
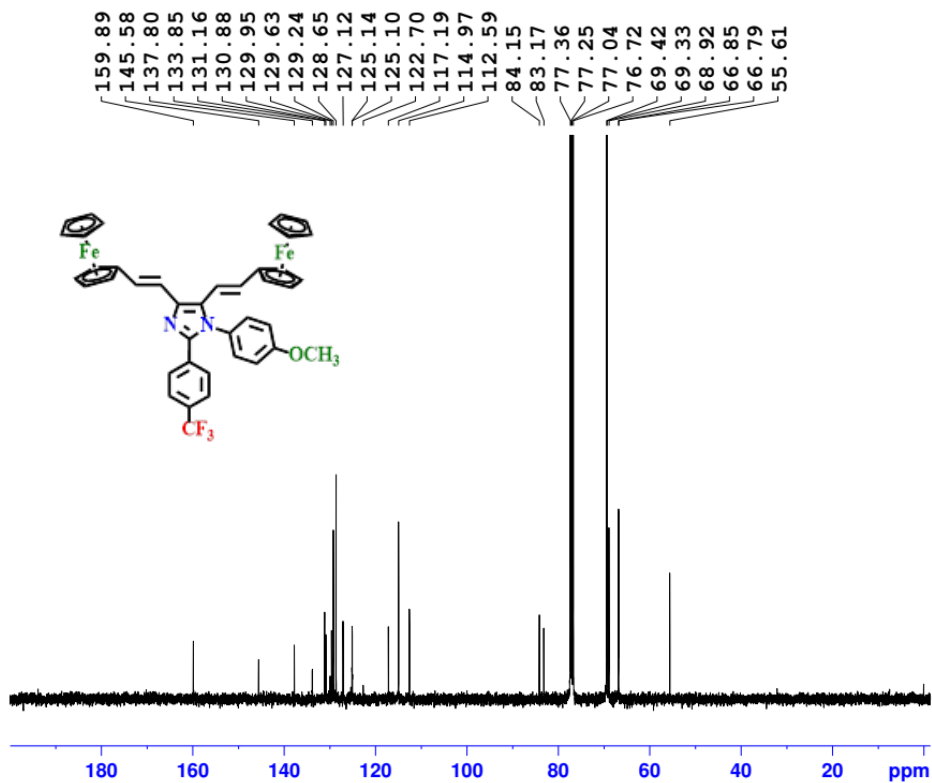**Figure S1.** ^{1}H NMR spectrum of chromophore **1** in CDCl$_3$ at 25 ^{o}C

Figure S2. ^{13}C NMR spectrum of chromophore **1** in CDCl$_3$ at 25 ^{o}C
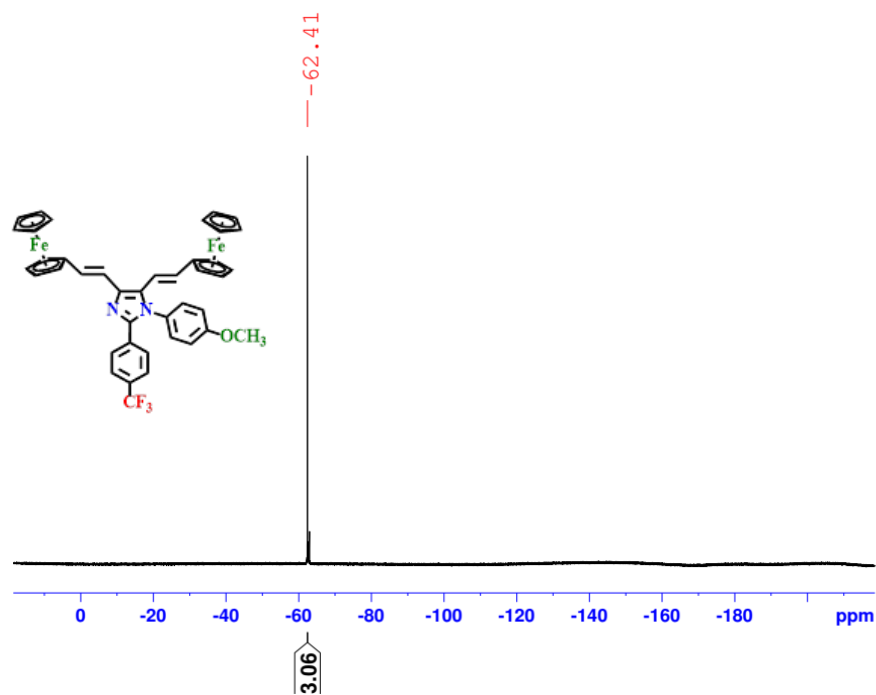
Figure S3. ^{19}F NMR spectrum of chromophore **1** in CDCl$_3$ at 25 ^{o}C
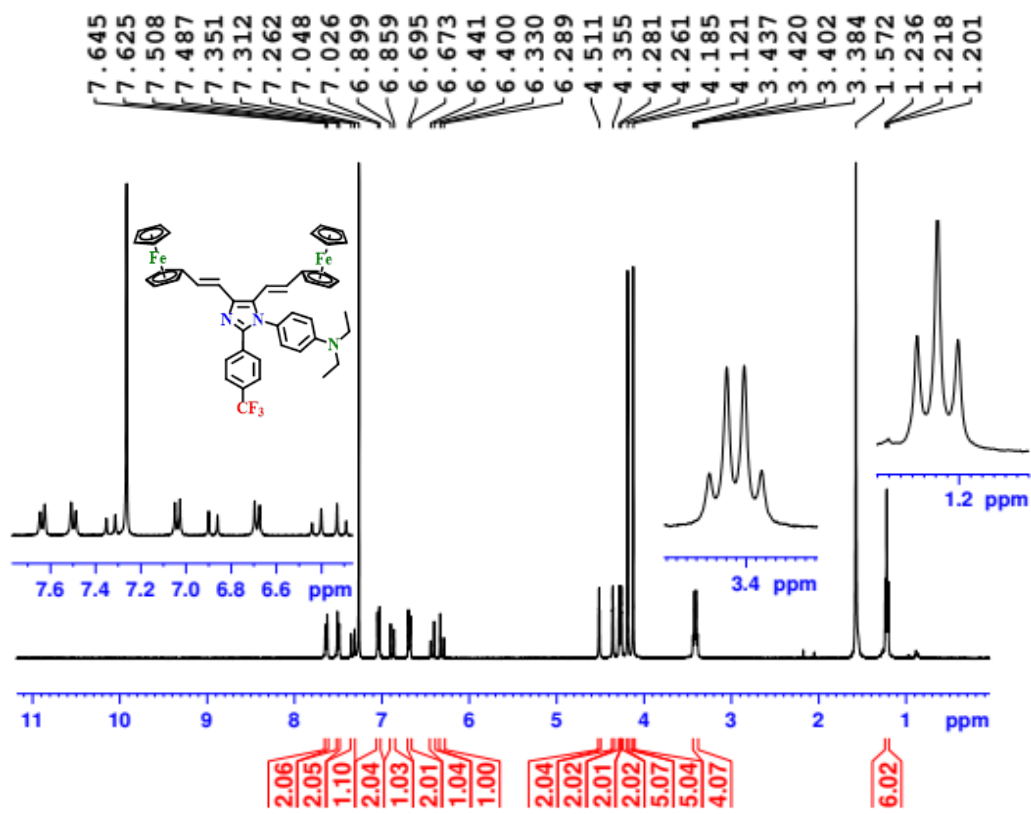
Figure S4. ^{1}H NMR spectrum of chromophore **2** in CDCl$_3$ at 25 ^{o}C

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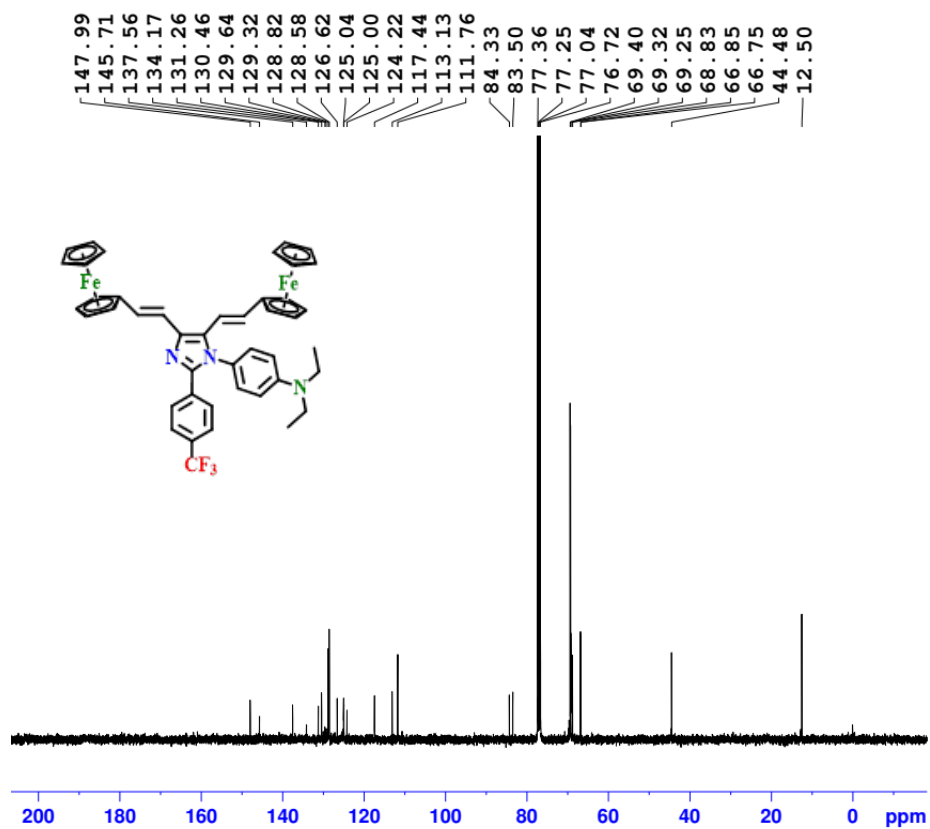
Figure S5. ^{13}C NMR spectrum of chromophore **2** in CDCl$_3$ at 25 °C
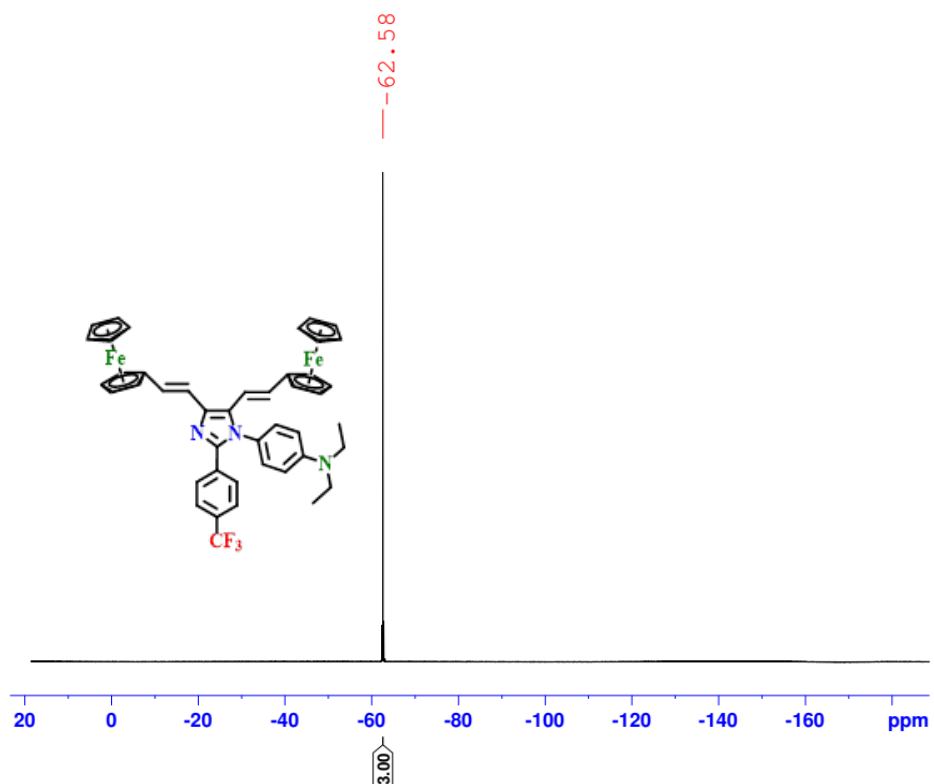

Figure S6. ^{19}F NMR spectrum of chromophore **2** in CDCl$_3$ at 25 °C
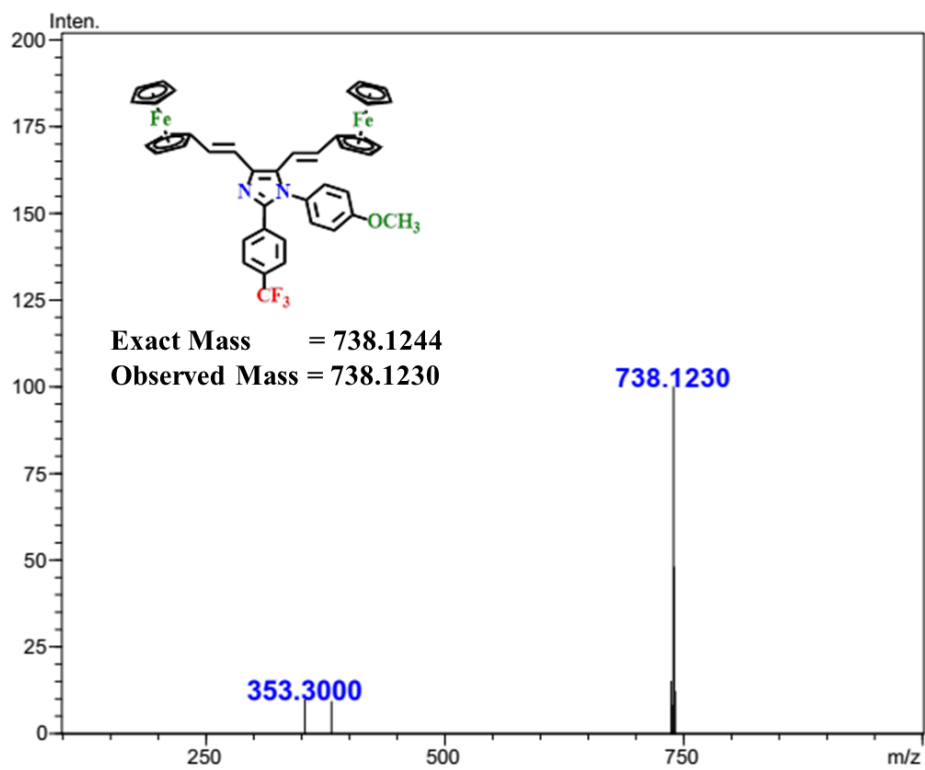
Figure S7. ESI-Mass spectrum of the chromophore **1**.
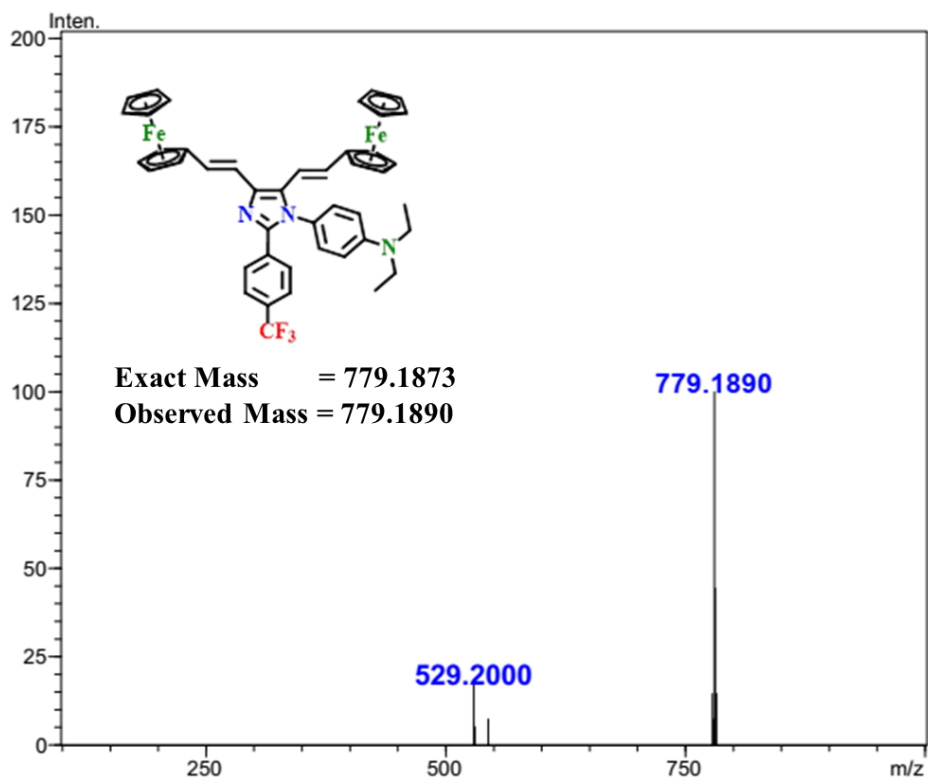

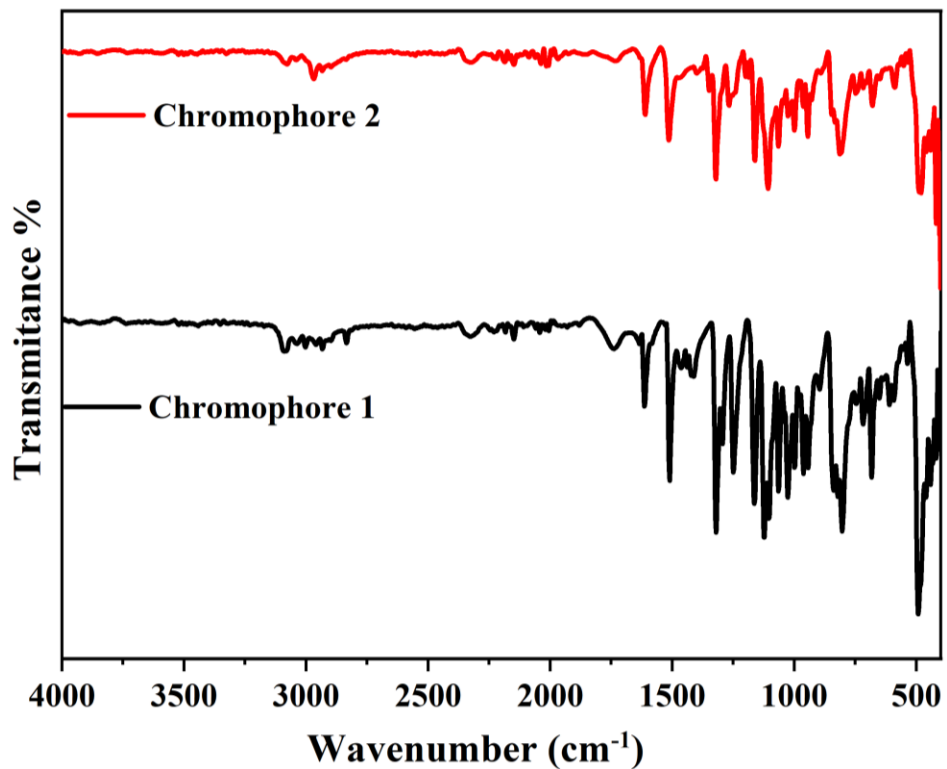**Figure S8.** ESI-Mass spectrum of the chromophore **2**.

Figure S9. FT-IR spectra of chromophores **1** and **2**.
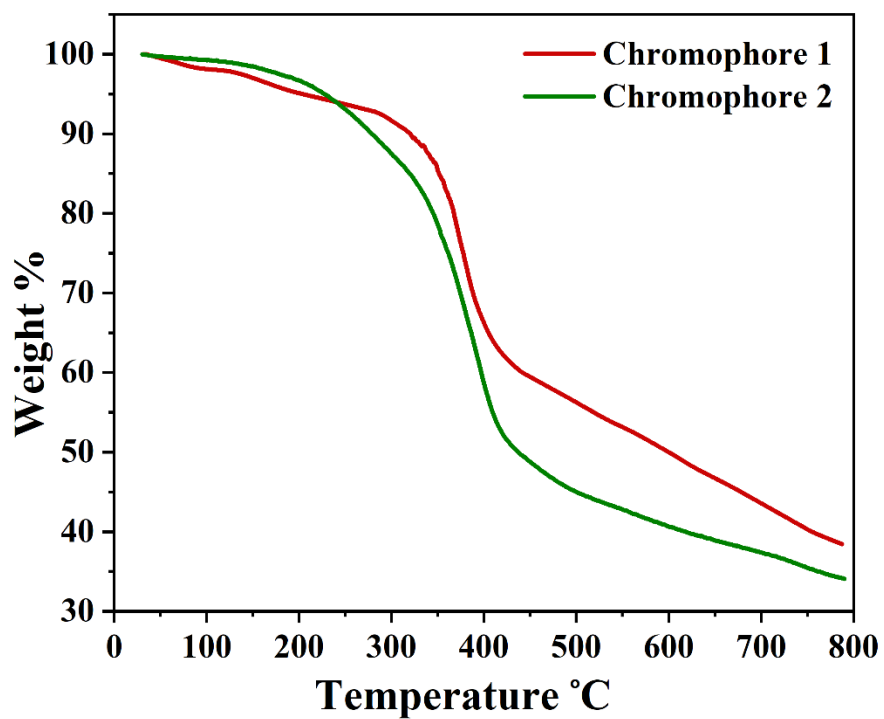
Figure S10. TGA curve of the chromophores **1** and **2**.
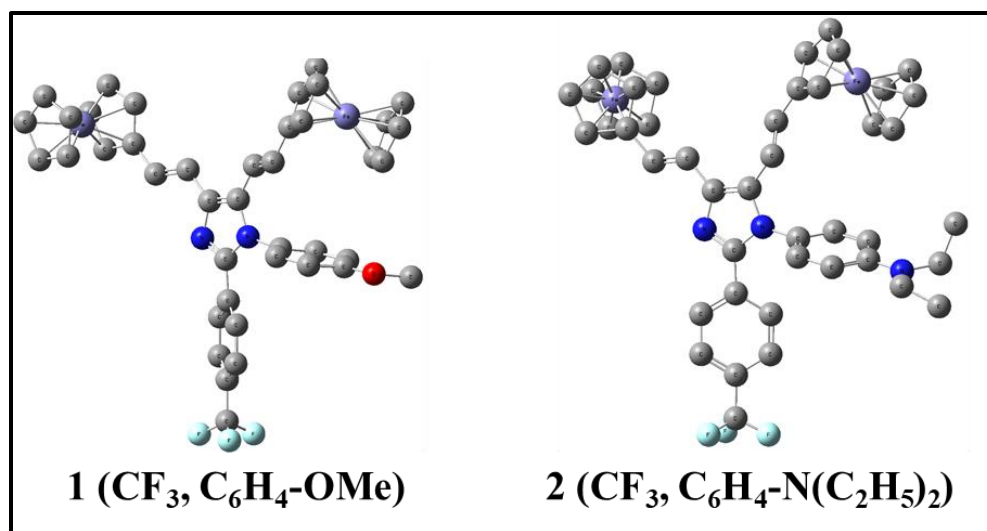
Figure S11. The optimized geometries of chromophores **1** and **2** obtained at B3LYP/6-31+G**
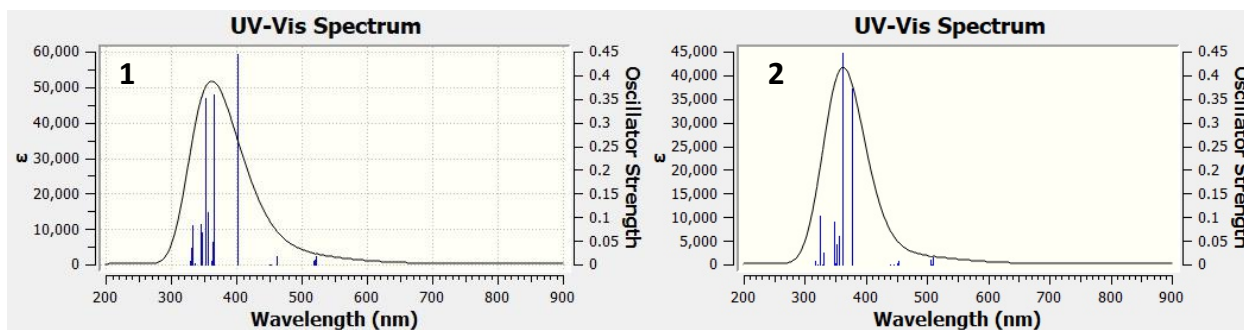level of theory

Figure S12. Theoretically calculated absorption spectra for the chromophores **1** and **2** with
$CHCl_3$ solvent. The absorption spectra were obtained by TD-DFT calculation with B3LYP/6-
31+G** level of theory. The spectra were visualized in Gauss View 6.1.

Table S1. Crystal data and structure refinement parameters for chromophores **1** and **2**.

Identification code	Chromophore 1	Chromophore 2
CCDC	1920307	1903164
Empirical formula	$C_{41}H_{33}F_3Fe_2N_2O$	$C_{44}H_{40}F_3Fe_2N_3$
Formula weight	738.39	779.49
Temperature, K	296 (2)	296 (2)
Wavelength, Å	0.71073	0.71073
Crystal System	Triclinic	Monoclinic
Space group	P -1	$P2_1/c$
Unit cell dimensions	a = 11.0840(13) Å	a = 16.097(2) Å
	b = 12.6976(19) Å	b = 22.892(4) Å
	c = 12.9135(18) Å	c = 10.3035(13) Å
	$\alpha = 80.552(6)°$	$\alpha = 90°$
	$\beta = 76.974(5)°$	$\beta = 101.194(5)°$
	$\gamma = 79.651(6)°$	$\gamma = 90°$
Volume	1727.3(4) A^3	3724.6(10) A^3
Z	2	4
Calculated density (Mg/m^3)	1.420	1.390
Absorption coefficient (mm^{-1})	0.891	0.829
F (000)	760	1616
Crystal size (mm^3)	0.300 x 0.200 x 0.200	0.350 x 0.350 x 0.300
Theta range for data collection (°)	2.25 to 28.28	1.57 to 23.00
Reflections collected	14137	30387
Completeness to theta = 25.242	99.1%	99.9 %
Max. and min. transmission	0.842 and 0.776	0.789 and 0.760
Goodness-of-fit on F^2	1.0459	1.0685
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Final R indices [$I > 2\sigma (I)$]	$R_1 = 0.0423$, $wR_2 = 0.1016$	$R_1 = 0.0546$, $wR_2 = 0.2008$
R indices (all data)	$R_1 = 0.0755$, $wR_2 = 0.1211$	$R_1 = 0.0924$, $wR_2 = 0.1164$

Table S2. Structural parameters for chromophores **1** and **2**

	1	2
Average Fe1-C	2.021	2.050
Average Fe1-C	2.091	2.044
Fe1-Cent(1)	1.640	1.644
Fe1-Cent(2)	1.654	1.639
Cent(1)-Fe(1)-Cent(2)	176.998	177.060
Average Fe2-C	2.064	2.032
Average Fe2-C	2.051	2.029
Fe2-Cent(1)	1.687	1.625
Fe2-Cent(2)	1.647	1.636
Cent(1)-Fe(2)-Cent(2)	177.866	176.165
C-F	1.191(5)	1.267(8)
O-C	1.429(5)	-
C-O-C	118.2(3)	-
C-N1-C	106.5(2)	106.3(4)
C-N2-C	106.7(2)	106.5(4)
C-C-C	123.7(3)	125.7(5)
C-C-C	129.6(3)	125.3(5)
The interatomic distances are reported in angstroms (Å); angles are (°)		

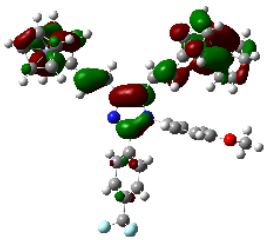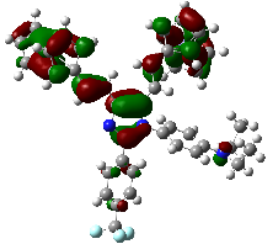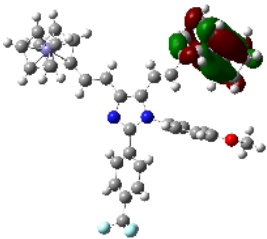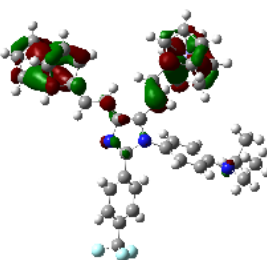**Table S3**. Selected torsion or dihedral (φ) angles of the chromophores **1** and **2**.
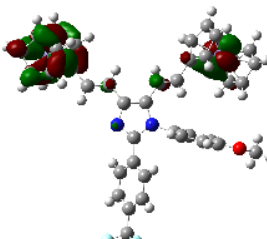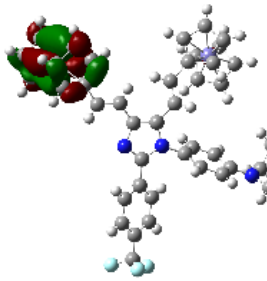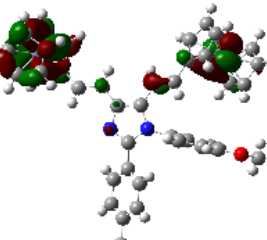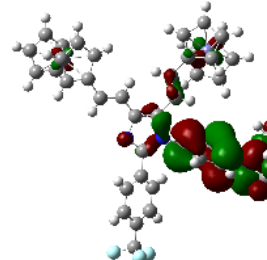
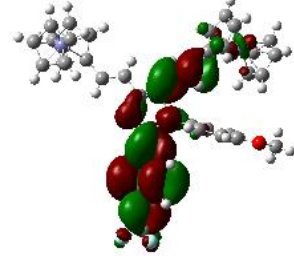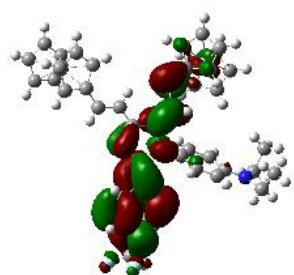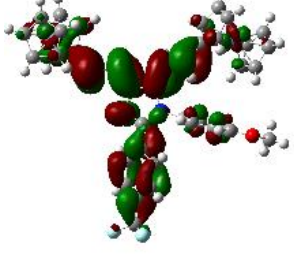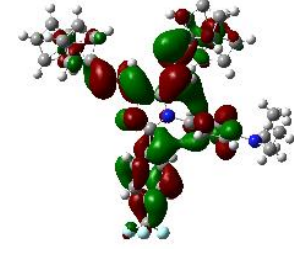| Chromophore **1**		Chromophore **2**	
Atoms	**Angles** (°)	**Atoms**	**Angles** (°)
C19-C18-C17-C16	-177.933	C8-C11-C12-C13	176.522
C29-C30-C31-C32	177.523	N1-C33-C34-C35	148.919
N1-C8-C5-C6	-147.398	N2-C33-C34-C39	149.866
N2-C8-C5-C4	-148.868	-	-
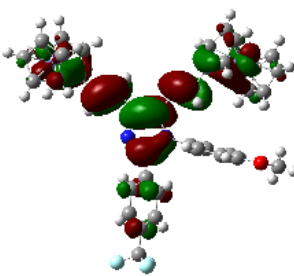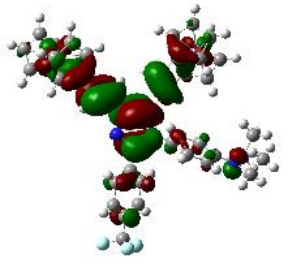
Table S4. Selected transitions obtained from TD-DFT calculation with B3LYP/6-31+G** level theory.

Entry	λ (nm)	Oscillator strength, f	Energy (eV)	Selected Major Transitions[a]
1 **(CF$_3$, C$_6$H$_4$-OMe)**	369	0.7363	3.35	H → L (67%)
	406	0.5596	3.04	H → L (91%)
	357	0.1784	3.47	H-5 → L+6 (18%), H-1 → L+2 (13%)
	346	0.0626	3.57	H-1 → L (75%)
	332	0.0546	3.73	H-4 → L (63%)
	344	0.0378	3.59	H-2 → L (78%)
	329	0.0330	3.75	H → L-+2 (69%)
	364	0.0220	3.40	H-3 → L (36%)
2 **(CF$_3$, C$_6$H$_4$-N(Et)$_2$)**	361	0.4032	3.42	H → L+1 (67%)
	377	0.3423	3.28	H → L (92%)
	358	0.1485	3.46	H-1 → L (76%)
	347	0.1030	3.56	H-2 → L+6 (12%)
	352	0.0220	3.52	H-5 → L+6 (18%), H-2 → L+1 (19%)
	353	0.0099	3.50	H-1 → L (13%)
	504	0.0096	2.45	H-2 → L+7 (29%)

[a]H = HOMO; L = LUMO; only contributions above 10% are included.

Table S5. Density surfaces of the frontier orbitals involved in electronic transitions of chromophores **1** and **2** which is derived from B3LYP/6-31+G** level of theory using isosurface value of 0.02 au.

Orbitals	1	2
HOMO-4		
HOMO-3		
HOMO-2		
HOMO-1		

HOMO		
LUMO		
LUMO+1		
LUMO+2		

LUMO+3		
LUMO+4		
LUMO+5		