Electronic Supplementary Information

Facile Intra- and Intermolecular Charge Transfer Control for Efficient Mechanofluorochromic Material

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Experimental section

Preparation of single crystal CN, F, and Me

Single crystal **CN**: vacuum dried pure sample of **CN** was taken in a vial and dissolved in $CHCl_3/n$-hexane (10:1) mixed solvent; by the slow evaporation at room temperature for about 4 weeks, a light brown **CN** single crystal was obtained. Single crystal **F** and **Me**: vacuum dried pure sample of **F** and **Me** was taken in a vial and dissolved in CH_2Cl_2/n-hexane (2:1) mixed solvent; by the slow evaporation at room temperature for about 4 weeks, pale yellow **F** and **Me** single crystal was obtained.

X-ray crystal structure analysis

The preliminary examination and data collection were performed using a Bruker SMART CCD detector system single-crystal X-ray di☐ractometer equipped with a sealed-tube X-ray source (50 kV × 30 mA) using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Preliminary unit cell constants were determined using a set of 45 narrow-frame (0.3° in ω) scans. The double pass method of scanning was used to exclude noise. Collected frames were integrated using an orientation matrix determined from narrow-frame scans. The SMART software package was used for data collection, and SAINT was used for frame integration.[1] Final cell constants were determined by global refinement of xyz centroids of reflections harvested from the entire data set. Structure solution and refinement were carried out using the SHELXTL-PLUS software package.[2] The crystallographic information has been deposited with the Cambridge Crystallographic Data Centre and assigned the CCDC code 2060789 for **CN**, 2060790 for **F**, 2060791 for **Me**.

Photophysical measurements

The UV/Vis absorption spectra were recorded using a Sinco Mega-2100 spectrophotometer in dual beam mode, and the fluorescence emission measurements were carried out using Shimadzu fluorometer (RF-6000) with a wavelength resolution of ~1 nm. Fluorescence lifetimes were measured by PicoQuant FluoTime 200 that takes advantage of the time-correlated single photon counting method. A pulsed diode laser operated at 20 MHz repetition rate was used as the excitation source. The FWHM of a laser pulse was typically 45 ps, and the instrument response function was ~190 ps when the Hamamatzu photomultiplier tube (H5783-01) was used. The emission quantum yields (Φ_f) were calculated using William's comparative method for samples of five different concentrations of (1–5) μM, using 9,10-diphenylanthracene (Φ_f = 0.95, ethanol) as a reference standard.[3]

Femtosecond transient absorption (fs-TA) measurements

The sub-picosecond time-resolved absorption spectra were collected using a pump–probe transient absorption spectroscopy system (Ultrafast Systems, Helios). The pump light was generated by using a

regenerative amplified titanium sapphire laser system (Spectra Physics, Spitfire Ace, 1 kHz) pumped by a diode-pumped Q-switched laser (Spectra Physics, Empower). The seed pulse was generated using a titanium sapphire laser (Spectra Physics, MaiTai SP). The pulses (340 nm) generated from an optical parametric amplifier (Spectra Physics, TOPAS prime) were used as the excitation pulse. And a white light continuum pulse, which was generated by focusing the residual of the fundamental light to a thin Sapphire crystal after the controlled optical delay, was used as a probe beam and directed to the sample cell with 2.0 mm of the optical path and detected with a CCD detector installed in the absorption spectroscope. The pump pulse was chopped by the mechanical chopper synchronized to one-half of the laser repetition rate, resulting in a pair of the spectra with and without the pump, from which the absorption change induced by the pump pulse was estimated.

Cyclic Voltammetry (CV)

A CH Instruments 701D potentiostat was used for electrochemical measurements, and cyclic voltammetry (CV) was performed in an electrolytic solution prepared using 1 mM of electroactive compounds and 0.1 M tetrabutylammonium perchlorate (Bu_4NClO_4) in deoxygenated dichloromethane. A three-electrode configuration, platinum wire, glassy carbon, and SCE were used as working, counter, and reference electrodes, respectively.

Density functional theory calculations

Density functional theory (DFT) calculations were performed by using Gaussian'16 software package. Full geometry optimizations in their ground state were performed using the B3LYP functional and the 6-31G (d, p) basis set for all atoms. The excitation energies and oscillator strengths for the lowest 100 singlet–singlet transitions at the optimized geometry in the ground state were obtained in time-dependent DFT (TD-DFT) calculations using the same basis set and functional as for the ground state. All Isodensity plots of the frontier orbitals were visualized by Chem3D Ultra and GaussView software.
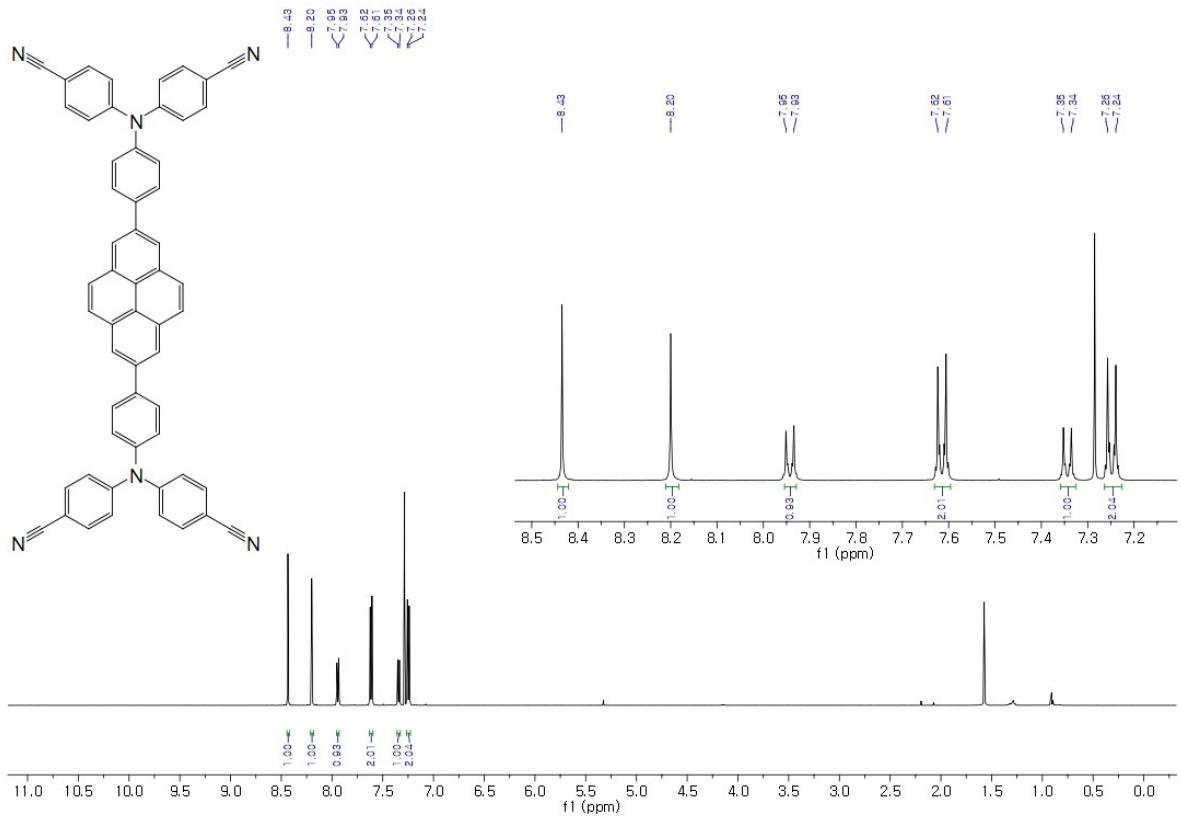
Figure S1. ^{1}H-NMR spectrum of **CN** in CDCl$_3$ (500MHz, 293K)
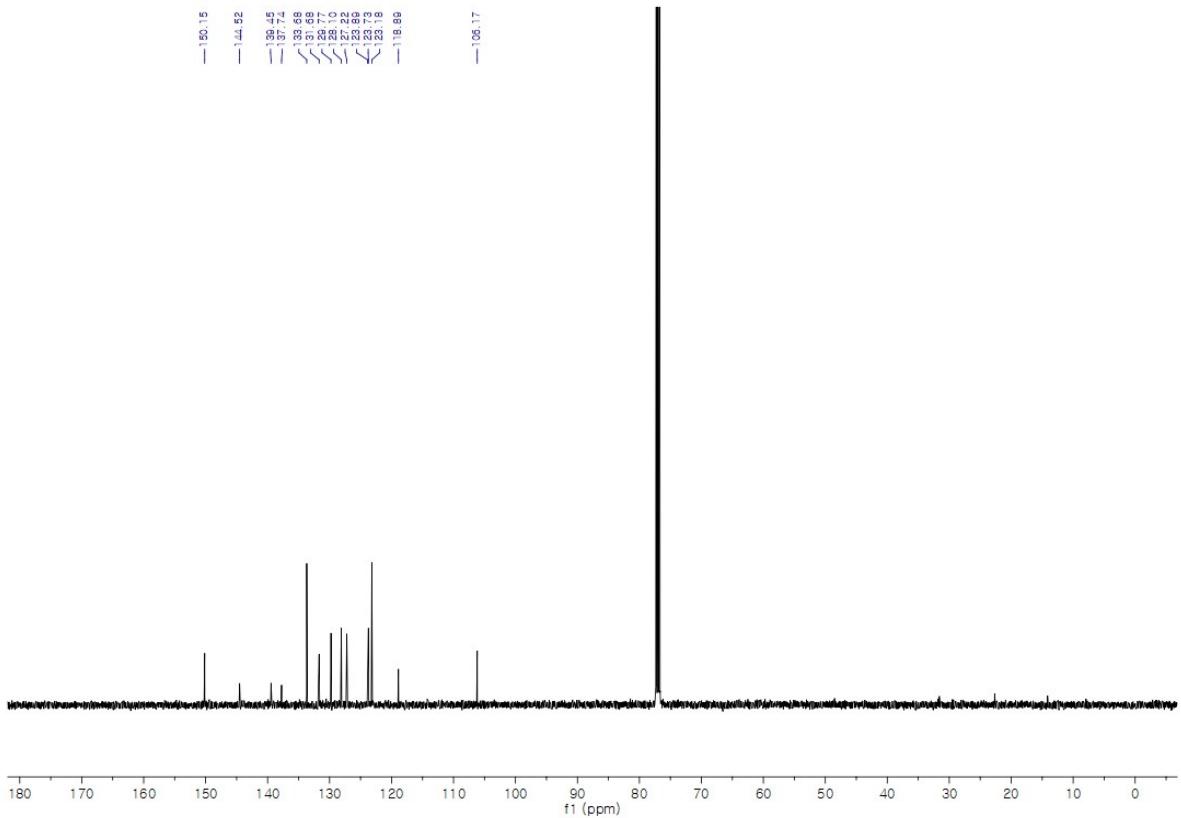
Figure S2. ^{13}C{^{1}H}-NMR spectrum of **CN** in CDCl$_3$ (125MHz, 293K)
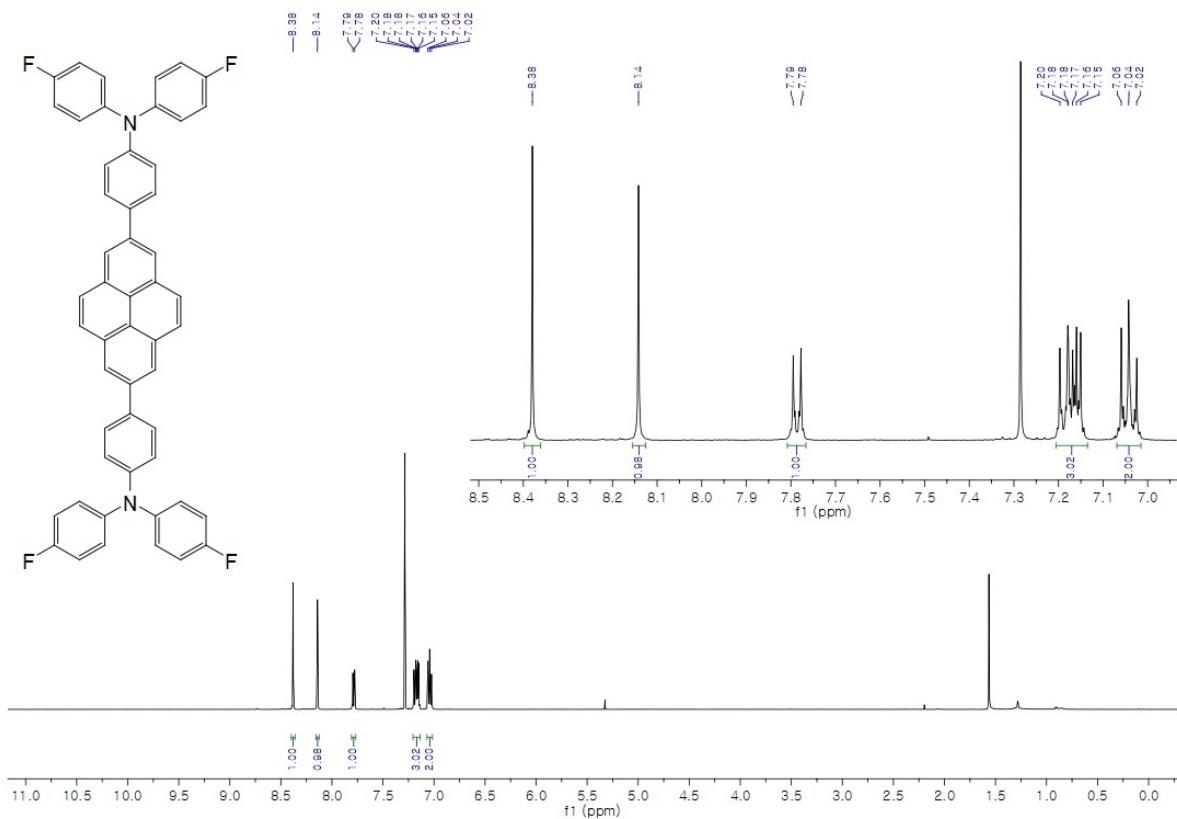
Figure S3. ^{1}H-NMR spectrum of **F** in CDCl$_3$ (500MHz, 293K)
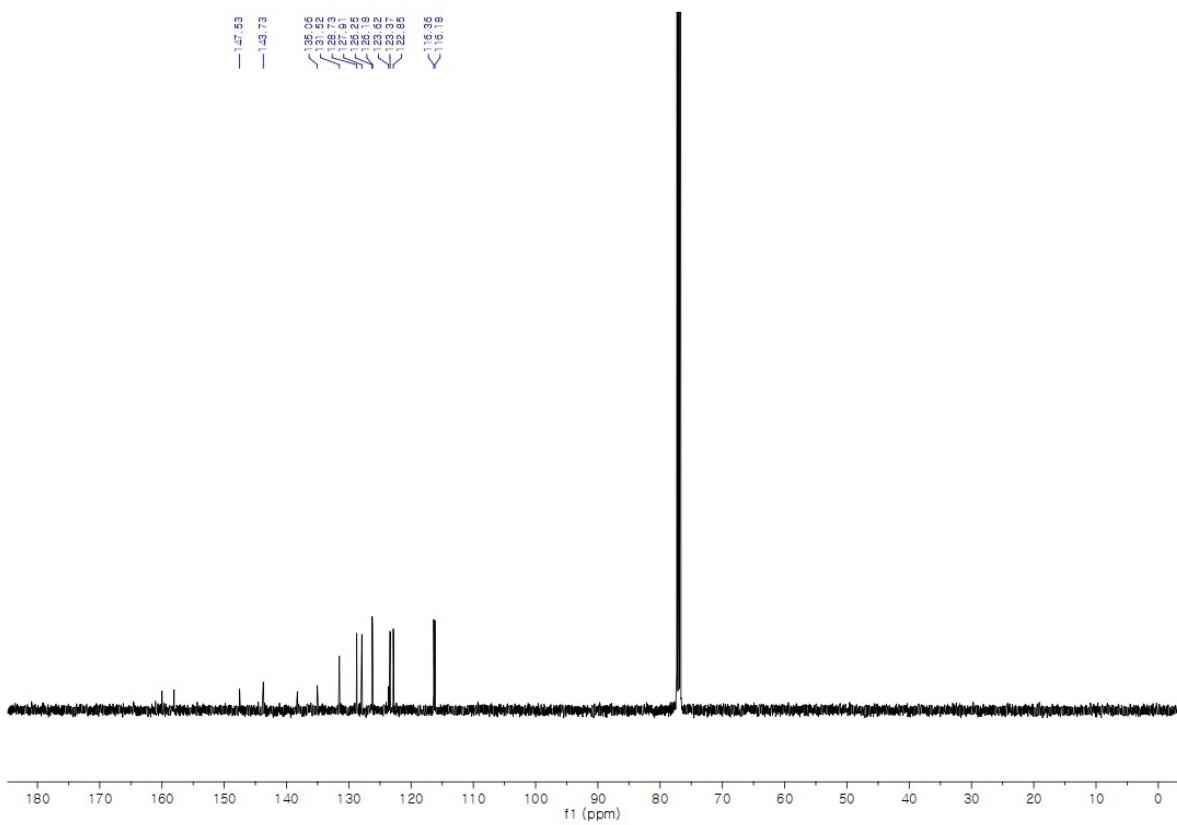
Figure S4. ^{13}C{^{1}H}-NMR spectrum of **F** in CDCl$_3$ (125MHz, 293K)
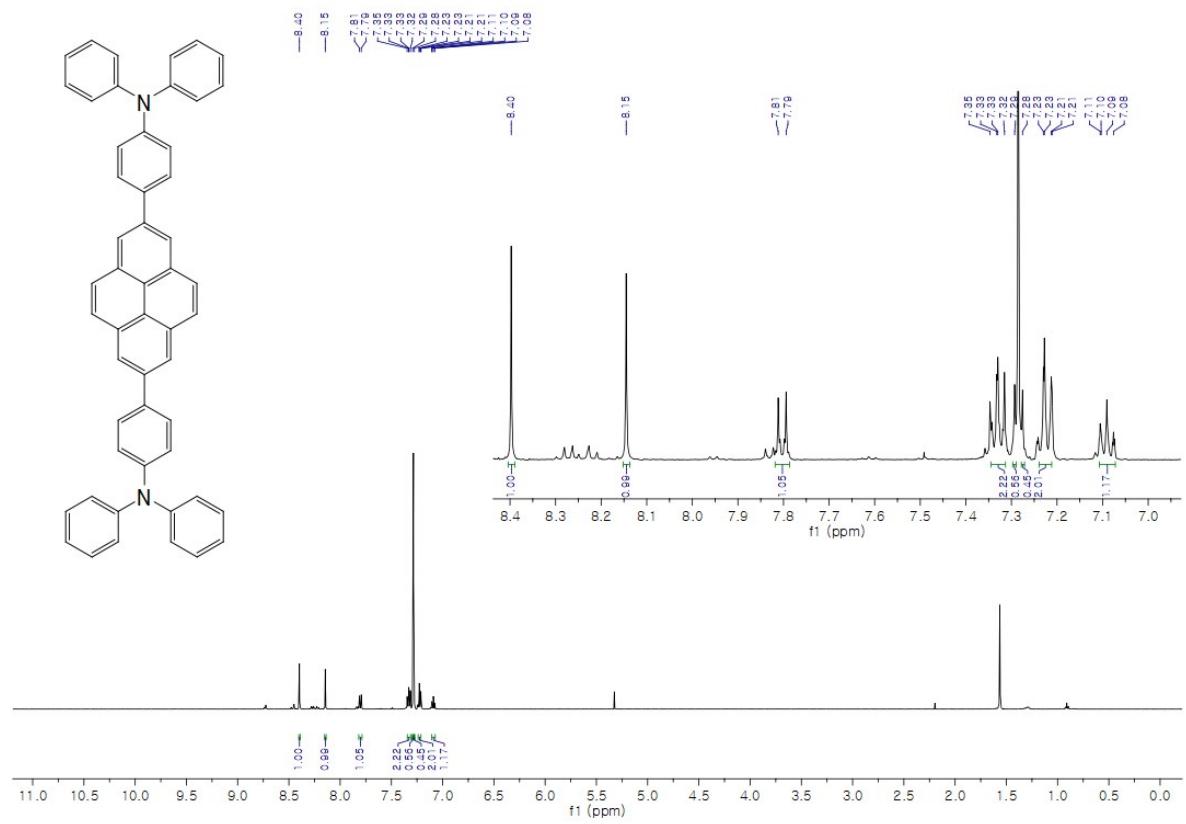
Figure S5. ^{1}H-NMR spectrum of **H** in CDCl$_3$ (500MHz, 293K)
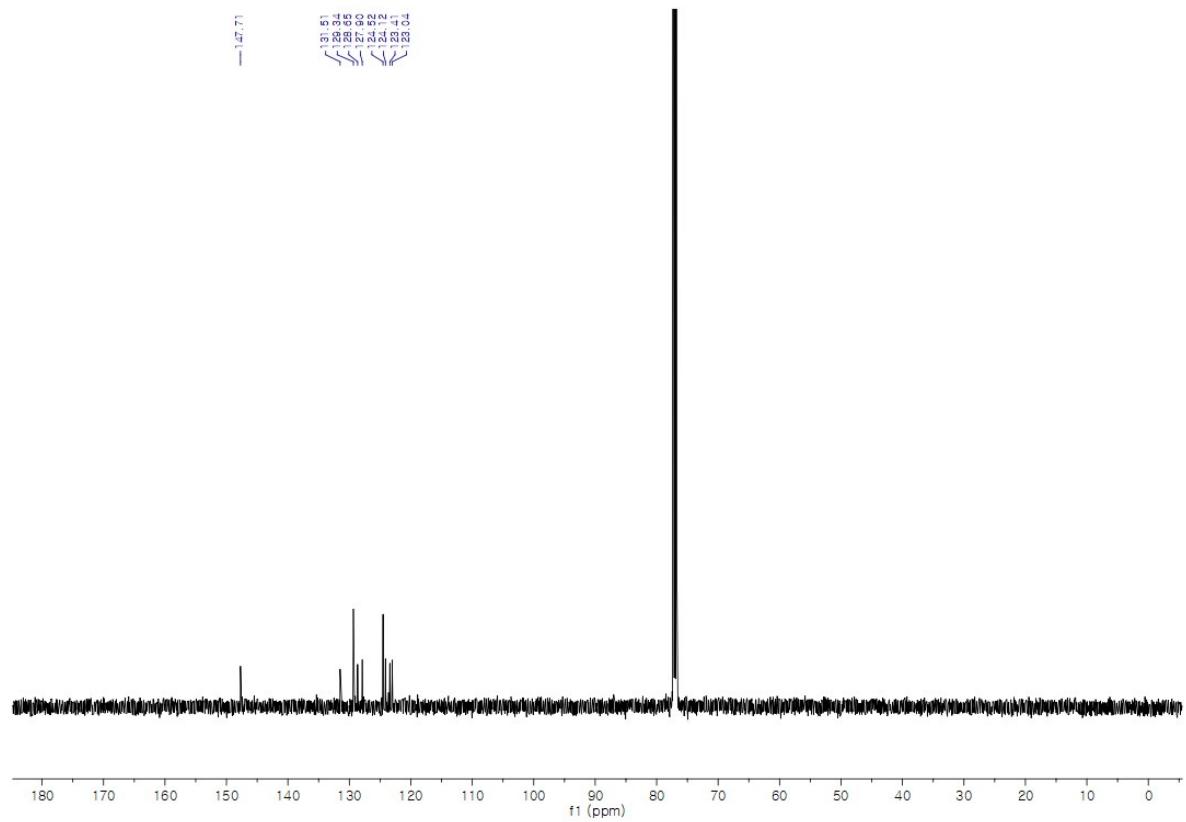
Figure S6. ^{13}C{^{1}H}-NMR spectrum of **H** in CDCl$_3$ (125MHz, 293K)
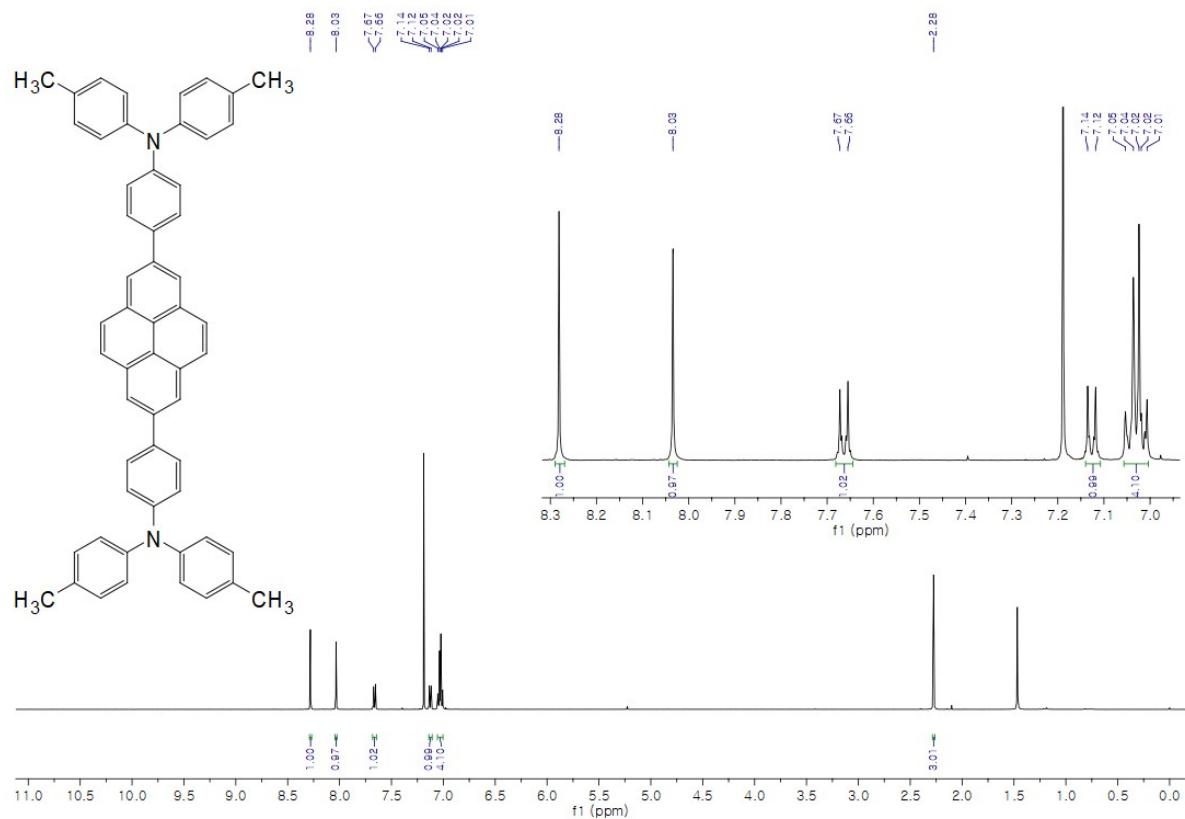
Figure S7. ^{1}H-NMR spectrum of **Me** in CDCl$_3$ (500MHz, 293K)
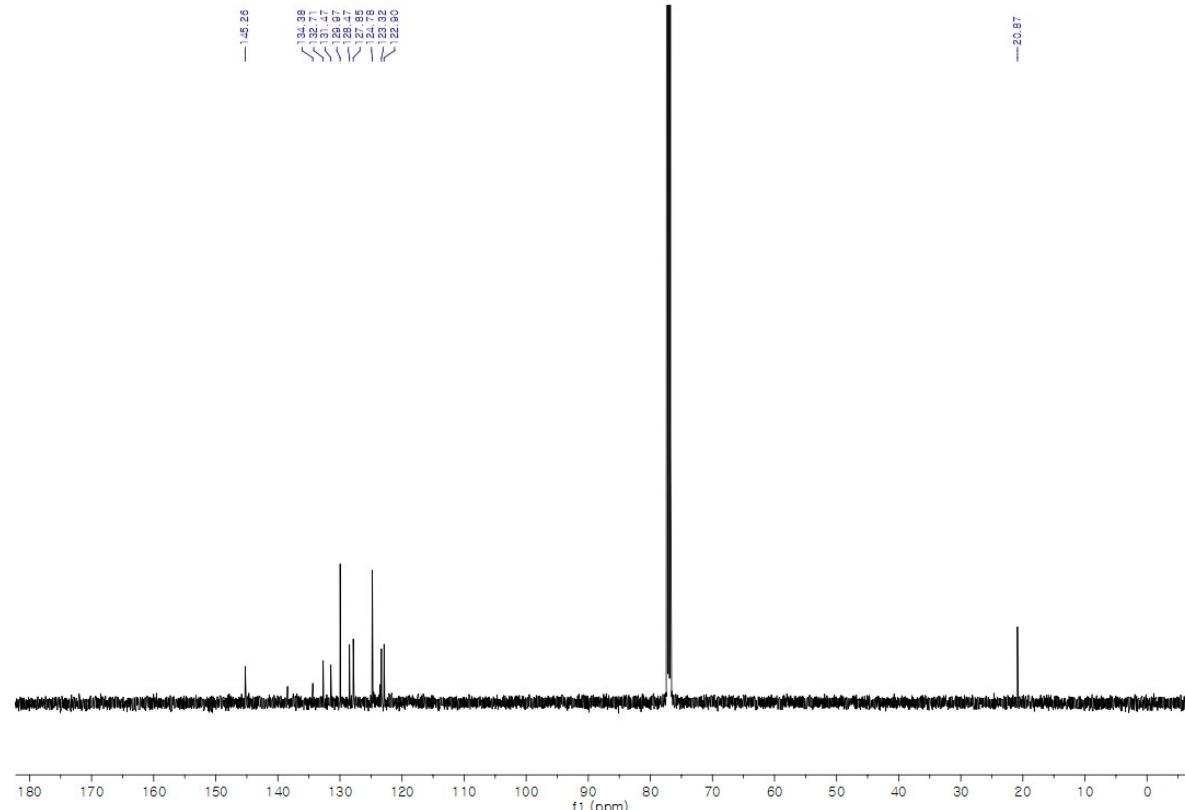
Figure S8. ^{13}C{^{1}H}-NMR spectrum of **Me** in CDCl$_3$ (125MHz, 293K)
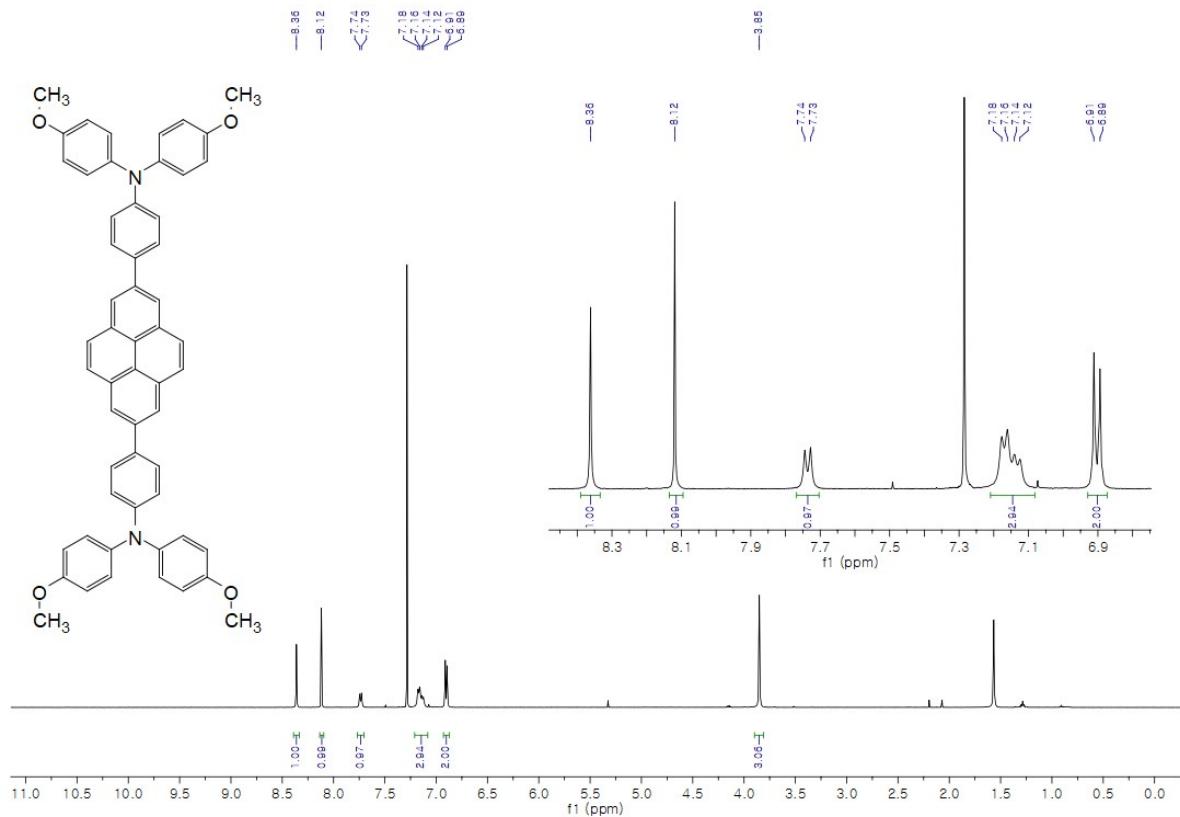
Figure S9. ^{1}H-NMR spectrum of **OMe** in CDCl$_3$ (500MHz, 293K)
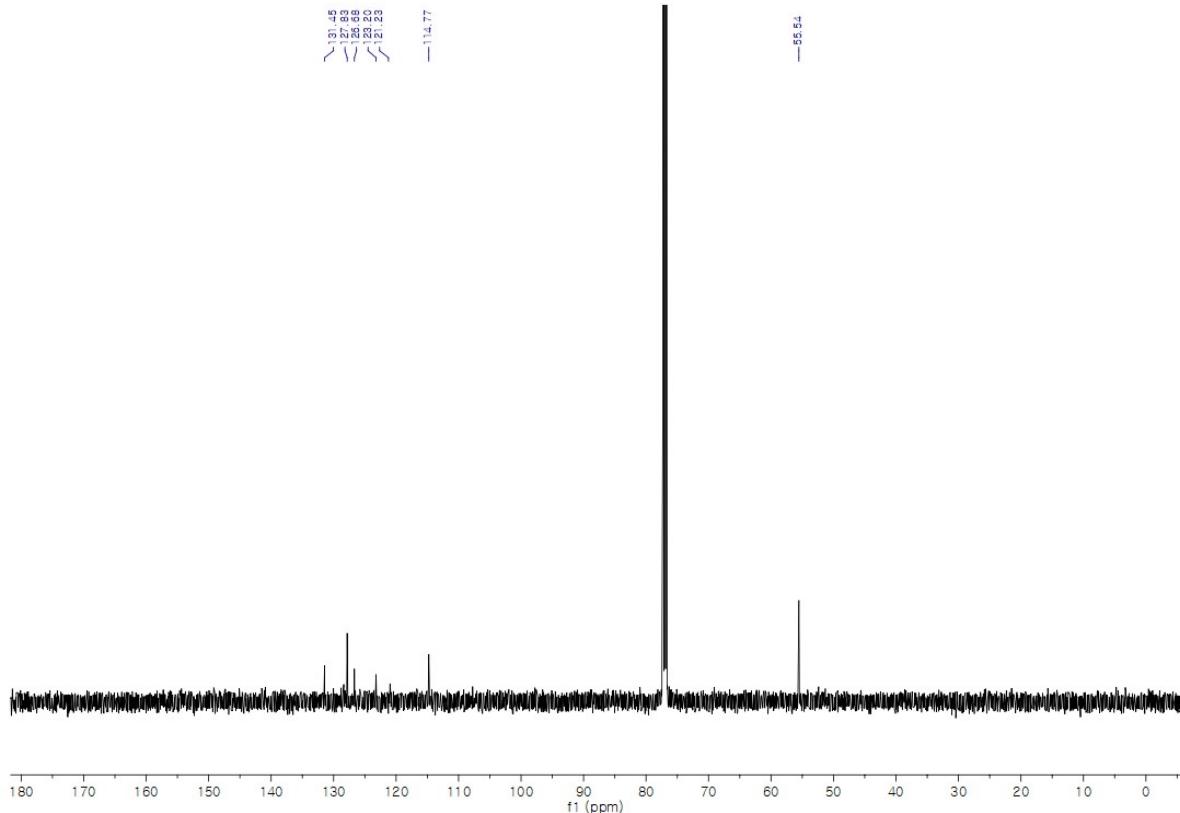
Figure S10. ^{13}C{^{1}H}-NMR spectrum of **OMe** in CDCl$_3$ (125MHz, 293K)
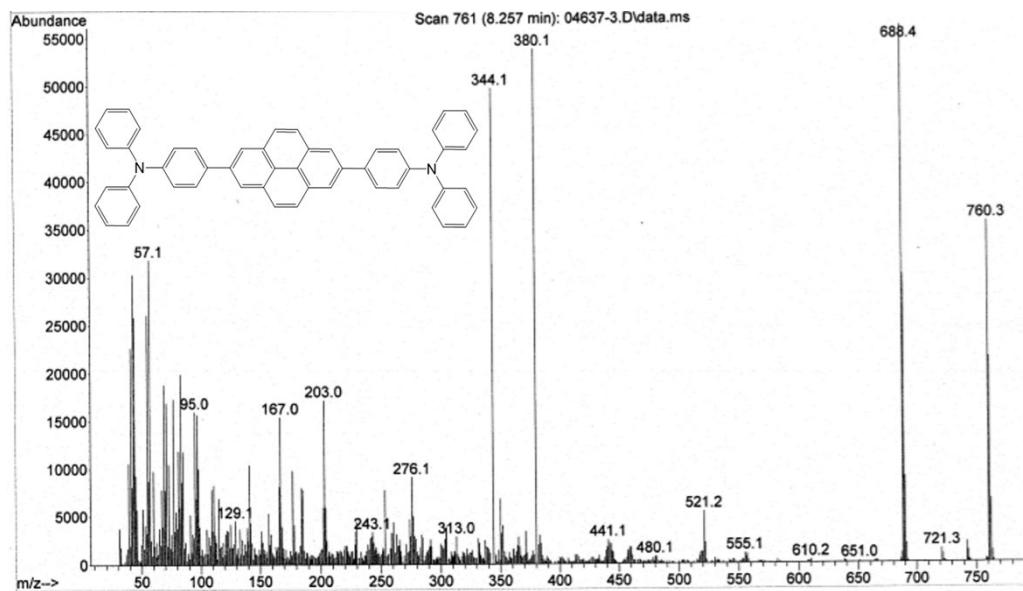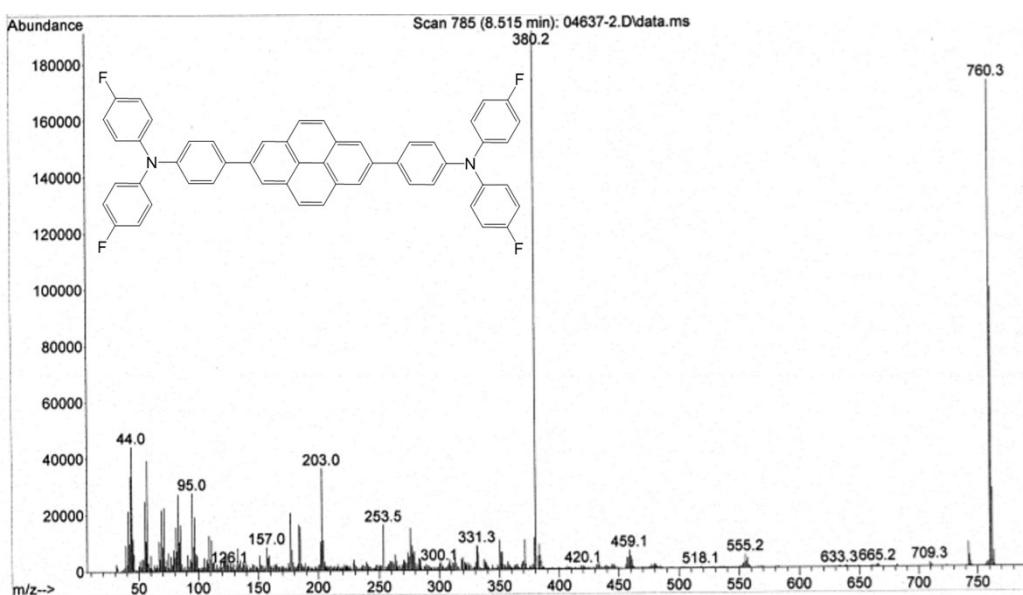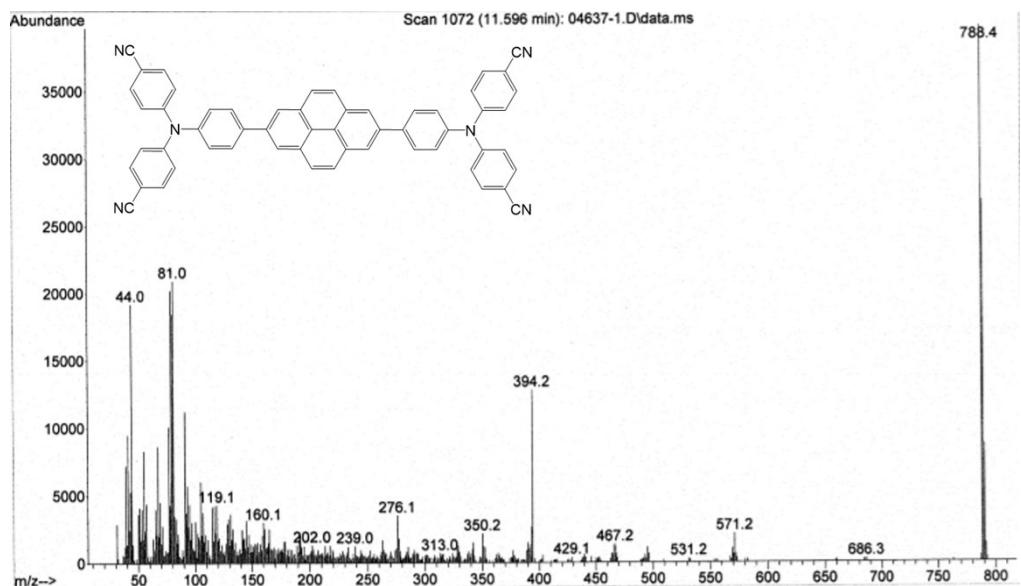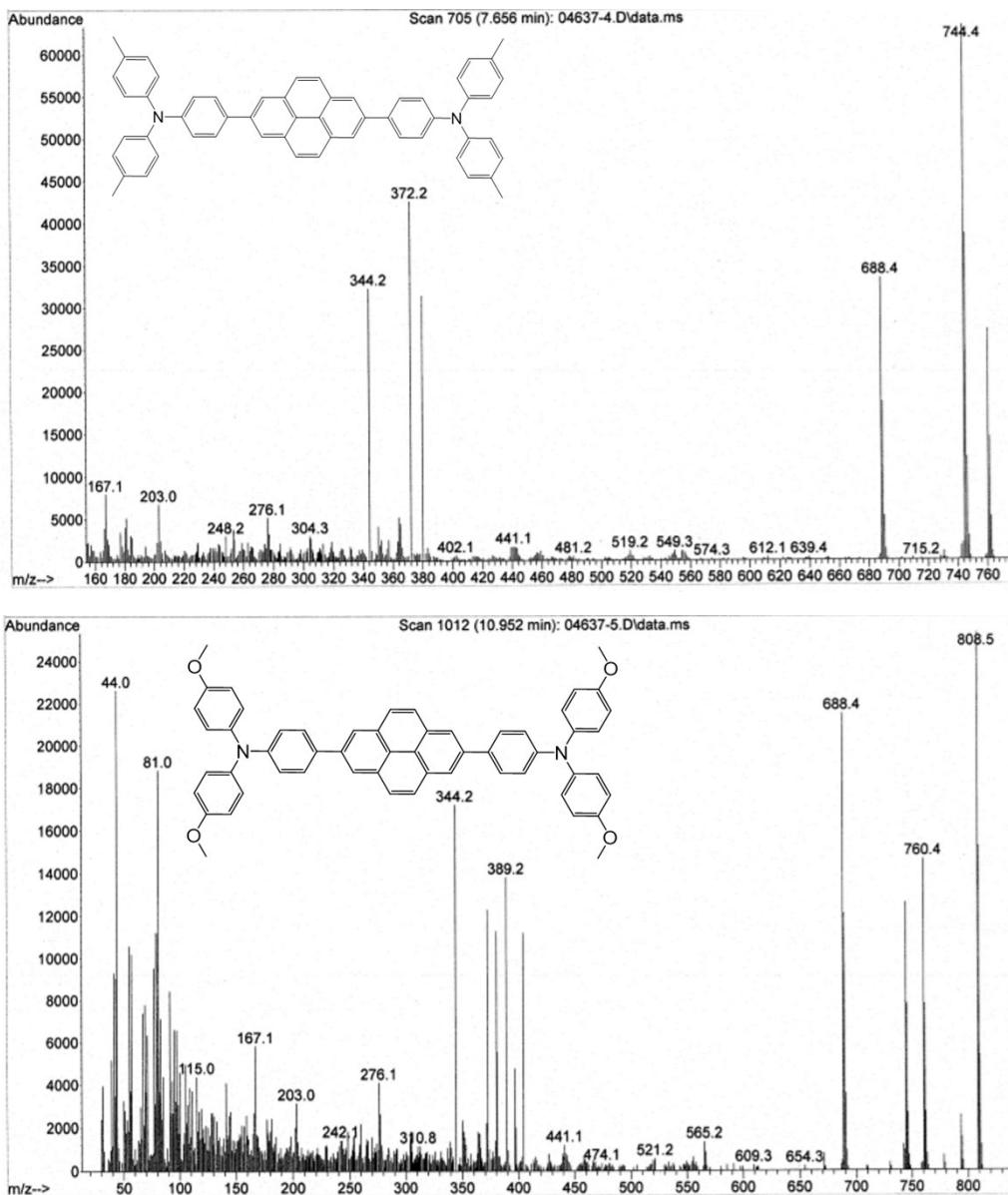
Figure S11. GC-MS data of **CN–OMe**.
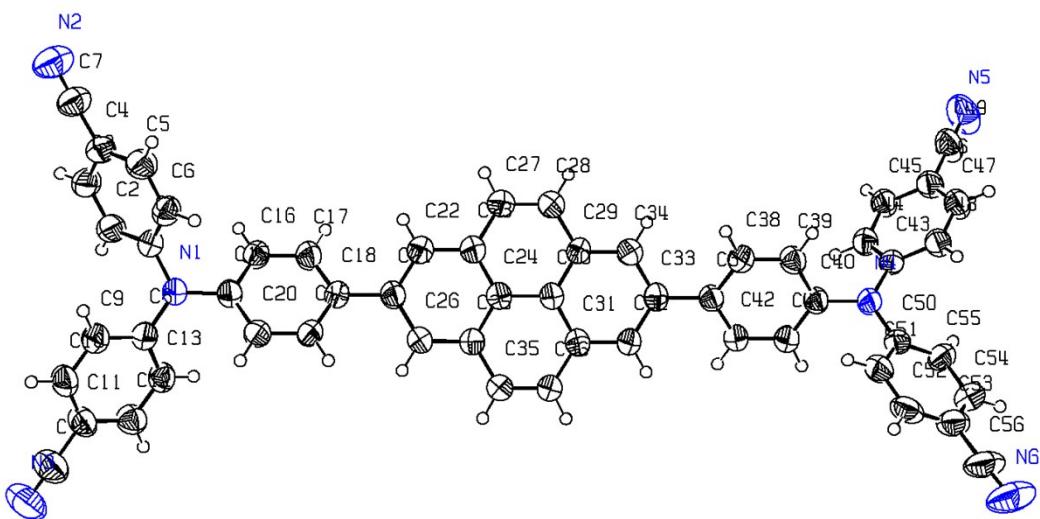
Figure S12. ORTEP drawings of **CN**. Ellipsoid contour percent probability level is 50%.
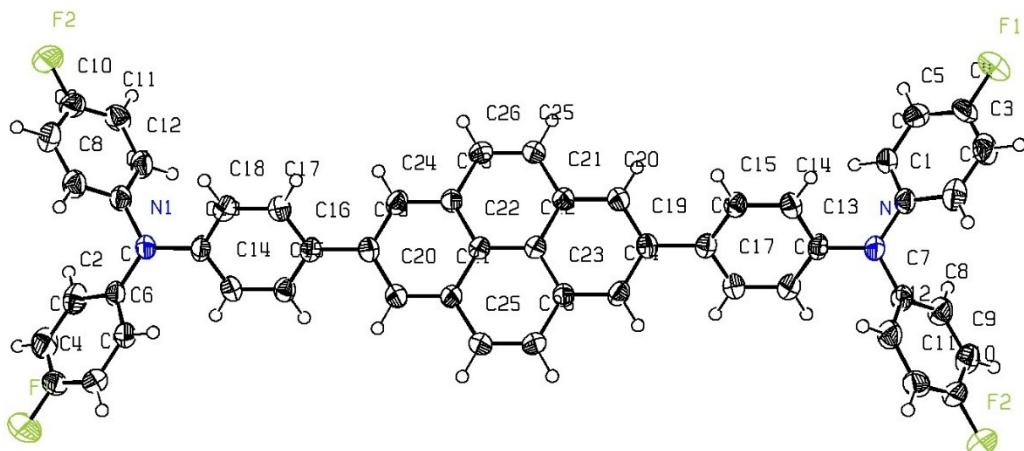
Figure S13. ORTEP drawings of **F**. Ellipsoid contour percent probability level is 50%.
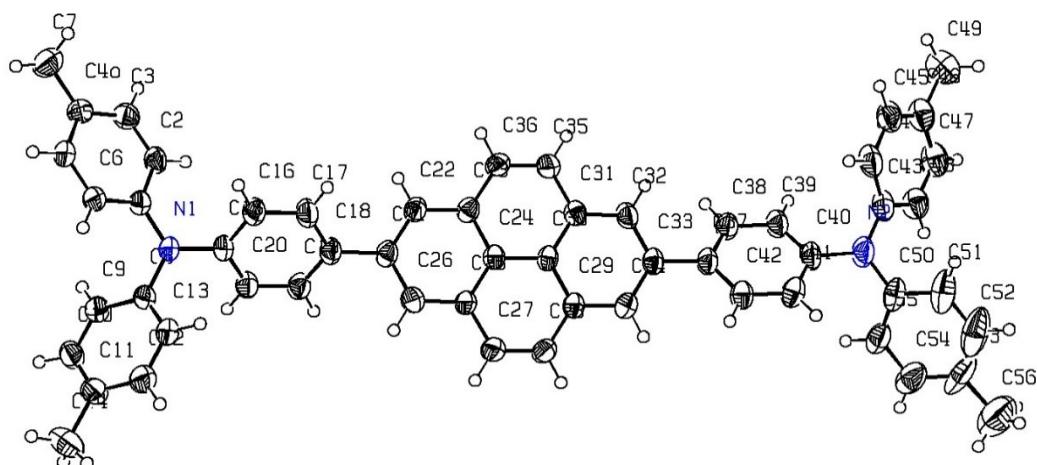
Figure S14. ORTEP drawings of **Me**. Ellipsoid contour percent probability level is 50%.

Table S1. Crystal data and structure refinement for **CN**

Comp.	CN	
Empirical formula	$C_{56} H_{32} N_6$	
Formula weight	788.87	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.275(11) Å	α = 92.33(4)°.
	b = 12.946(14) Å	β = 96.81(5)°.
	c = 20.99(3) Å	γ = 92.08(5)°.
Volume	2499(5) Å^3	
Z	2	
Density (calculated)	1.049 Mg/m^3	
Absorption coefficient	0.063 mm^{-1}	
F(000)	820	
Crystal size	0.198 x 0.092 x 0.050 mm^3	
Theta range for data collection	1.956 to 26.000°.	
Index ranges	-11<=h<=11, -15<=k<=15, -25<=l<=25	
Reflections collected	53139	
Independent reflections	9813 [R(int) = 0.0819]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7457 and 0.6949	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9813 / 0 / 559	
Goodness-of-fit on F^2	1.032	
Final R indices [I>2sigma(I)]	R1 = 0.0720, wR2 = 0.1955	
R indices (all data)	R1 = 0.1665, wR2 = 0.2692	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.231 and -0.226 e.Å^{-3}	

Table S2. Crystal data and structure refinement for **F**

Comp.	**F**	
Empirical formula	$C_{52} H_{32} F_4 N_2$	
Formula weight	760.79	
Temperature	223(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 10.7743(11) Å	$\alpha = 90°$.
	b = 11.1285(13) Å	$\beta = 108.374(2)°$.
	c = 16.6643(19) Å	$\gamma = 90°$.
Volume	1896.2(4) $Å^3$	
Z	2	
Density (calculated)	1.332 Mg/m^3	
Absorption coefficient	0.091 mm^{-1}	
F(000)	788	
Crystal size	0.254 x 0.143 x 0.051 mm^3	
Theta range for data collection	2.238 to 28.282°.	
Index ranges	-14<=h<=14, -14<=k<=14, -22<=l<=22	
Reflections collected	55633	
Independent reflections	4705 [R(int) = 0.1727]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7457 and 0.6630	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4705 / 0 / 262	
Goodness-of-fit on F^2	1.034	
Final R indices [I>2sigma(I)]	R1 = 0.0843, wR2 = 0.1445	
R indices (all data)	R1 = 0.1732, wR2 = 0.1743	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.186 and -0.253 e.$Å^{-3}$	

Table S3. Crystal data and structure refinement for **Me**

Comp.	**Me**	
Empirical formula	$C_{56} H_{44} N_2$	
Formula weight	744.93	
Temperature	223(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 36.361(3) Å	$\alpha = 90°$.
	b = 7.2580(6) Å	$\beta = 110.615(2)°$.
	c = 33.477(3) Å	$\gamma = 90°$.
Volume	8268.9(12) $Å^3$	
Z	8	
Density (calculated)	1.197 Mg/m^3	
Absorption coefficient	0.069 mm^{-1}	
F(000)	3152	
Crystal size	0.242 x 0.109 x 0.019 mm^3	
Theta range for data collection	2.287 to 26.003°.	
Index ranges	-44<=h<=44, -8<=k<=8, -41<=l<=41	
Reflections collected	113454	
Independent reflections	8096 [R(int) = 0.2080]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7453 and 0.6737	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8096 / 6 / 527	
Goodness-of-fit on F^2	1.018	
Final R indices [I>2sigma(I)]	R1 = 0.0661, wR2 = 0.1422	
R indices (all data)	R1 = 0.1757, wR2 = 0.1931	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.402 and -0.340 e.$Å^{-3}$	
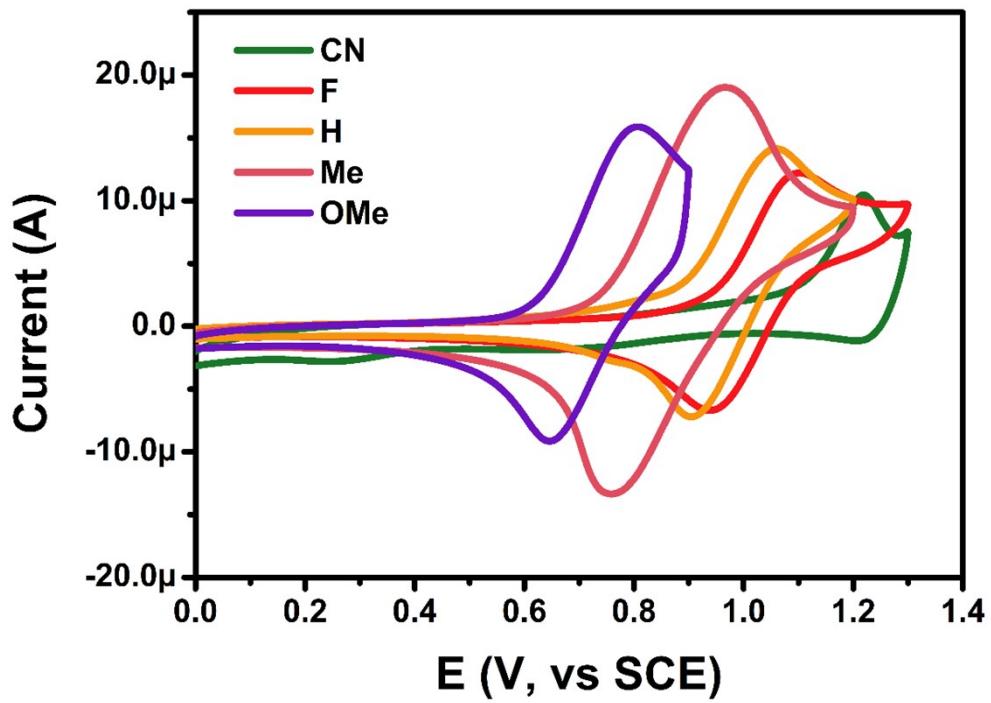
Figure S15. CV curves of **CN–OMe** in CH_2Cl_2 solution containing 0.1 M TBAP as electrolyte, at a scan rate of 0.1 Vs^{-1}.
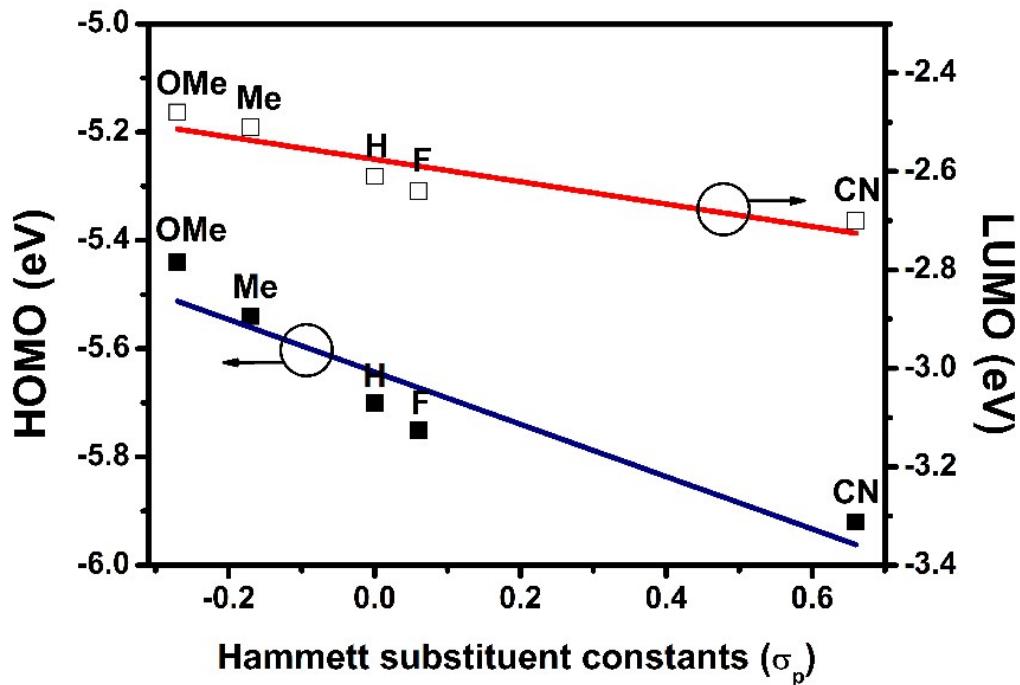
Figure S16. Plots of experimental HOMO (■) and LUMO (□) levels versus the Hammett substituent constants (σ_p).

Table S4. Energy band gap properties of **CN**, **F**, **H**, **Me**, and **OMe**.

	$HOMO^a$ (eV)	$LUMO^b$ (eV)	E_g^{opt} (eV)	$HOMO^c$ (eV)	$LUMO^c$ (eV)	E_g^{cal} (eV)
CN	-5.92	-2.70	3.22	-5.77	-2.01	3.76
F	-5.75	-2.64	3.11	-5.00	-1.58	3.42
H	-5.70	-2.61	3.09	-4.88	-1.49	3.39
Me	-5.54	-2.51	3.03	-4.73	-1.43	3.30
OMe	-5.44	-2.48	2.96	-4.55	-1.39	3.16

$_a E_{HOMO}(eV) = -e(E_{onset}^{ox} + 4.8)$. $_b E_{LUMO}(eV) = -e(E_{HOMO} + E_g^{opt})$. ^{c} Obtained by DFT calculation.
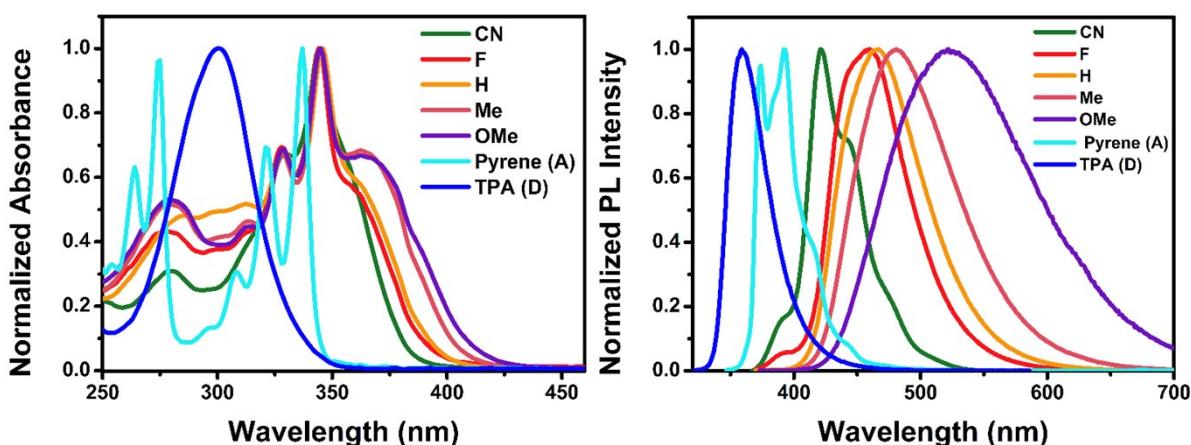
Figure S17. (top): UV-vis absorption spectra in CH_2Cl_2 solution of TPA, Py and **CN–OMe**. (bottom): emission spectra in CH_2Cl_2 solution of TPA, Py, and **CN–OMe**.

Table S5. Absorption and molar extinction coefficients of **CN–OMe** in CH_2Cl_2 at 5 μM concentration.

	Absorption (nm)	Molar extinction coefficients (M^{-1} cm^{-1})
CN	279, 329, 344, 357	48327, 106251, 157815, 101468
F	278, 328, 344, 360	35874, 57809, 83588, 46418
H	283, 328, 345, 362	58991, 84669, 123213, 71849
Me	278, 328, 345, 363	64286, 83681, 124283, 84766
OMe	279, 328, 345, 365	57743, 74844, 109158, 72224
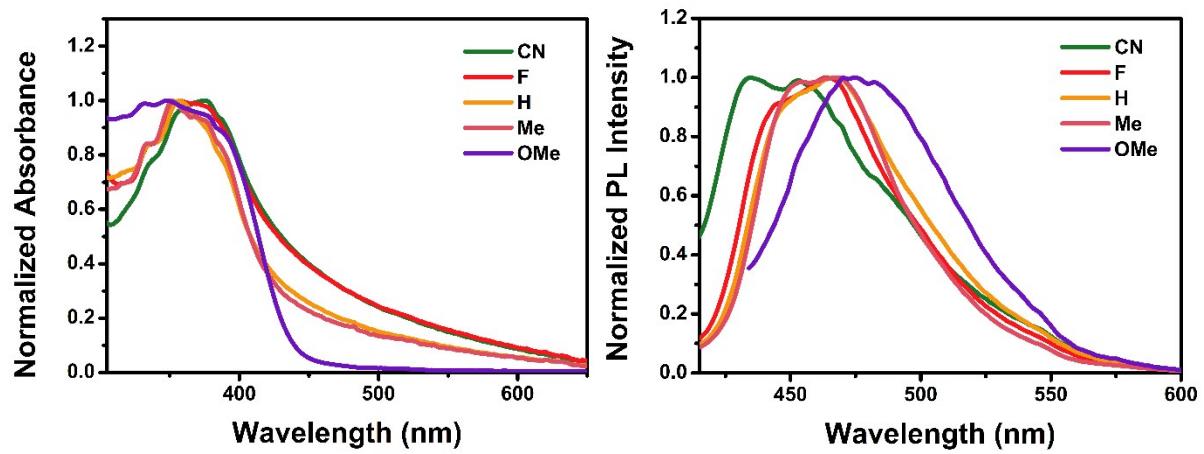
Figure S18. UV-vis absorption (left) and emission (right) spectra of **CN–OMe** in the solid state.
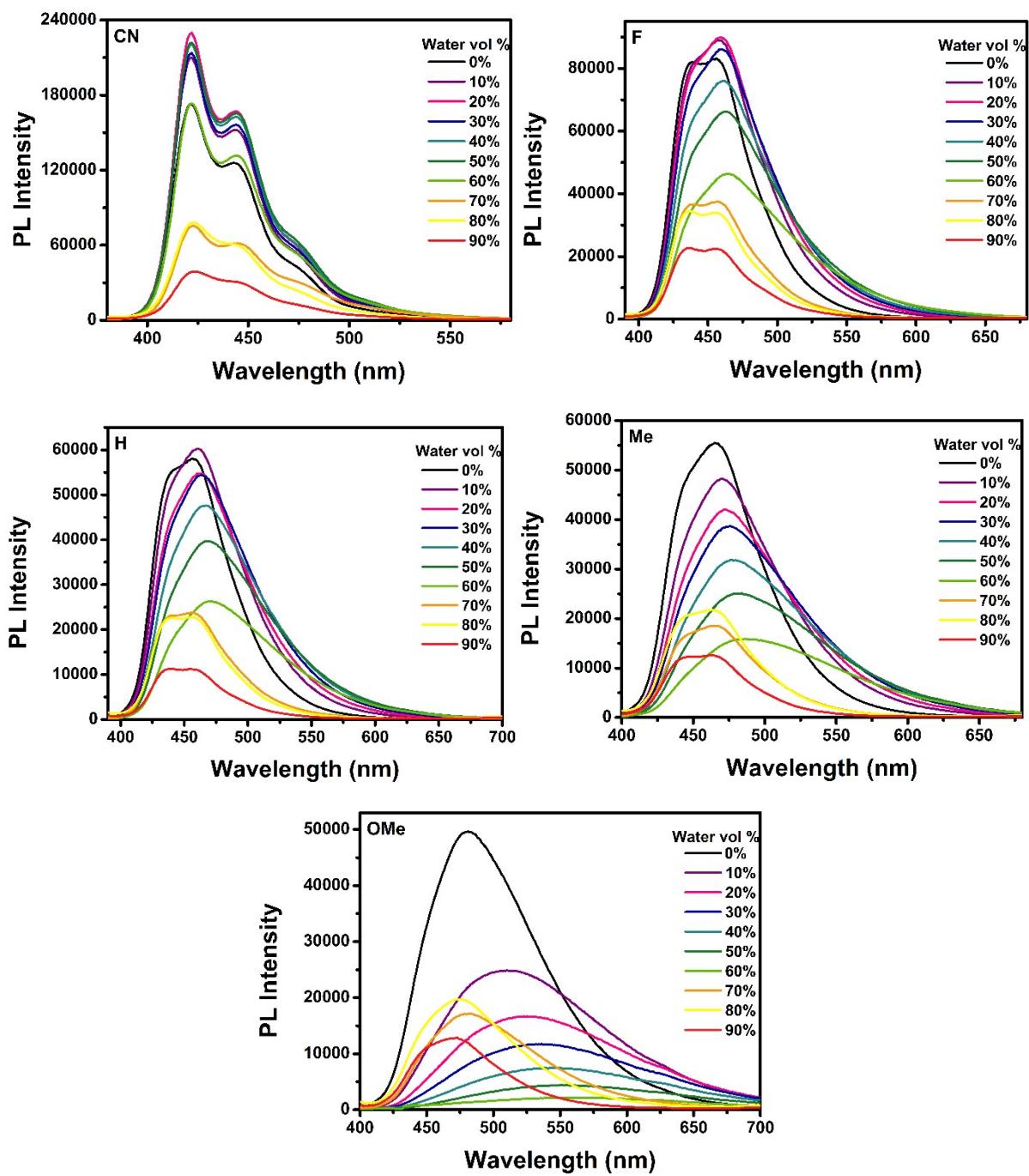
Figure S19. Emission spectra of **CN–OMe** in THF/H$_2$O mixtures with different f_w.
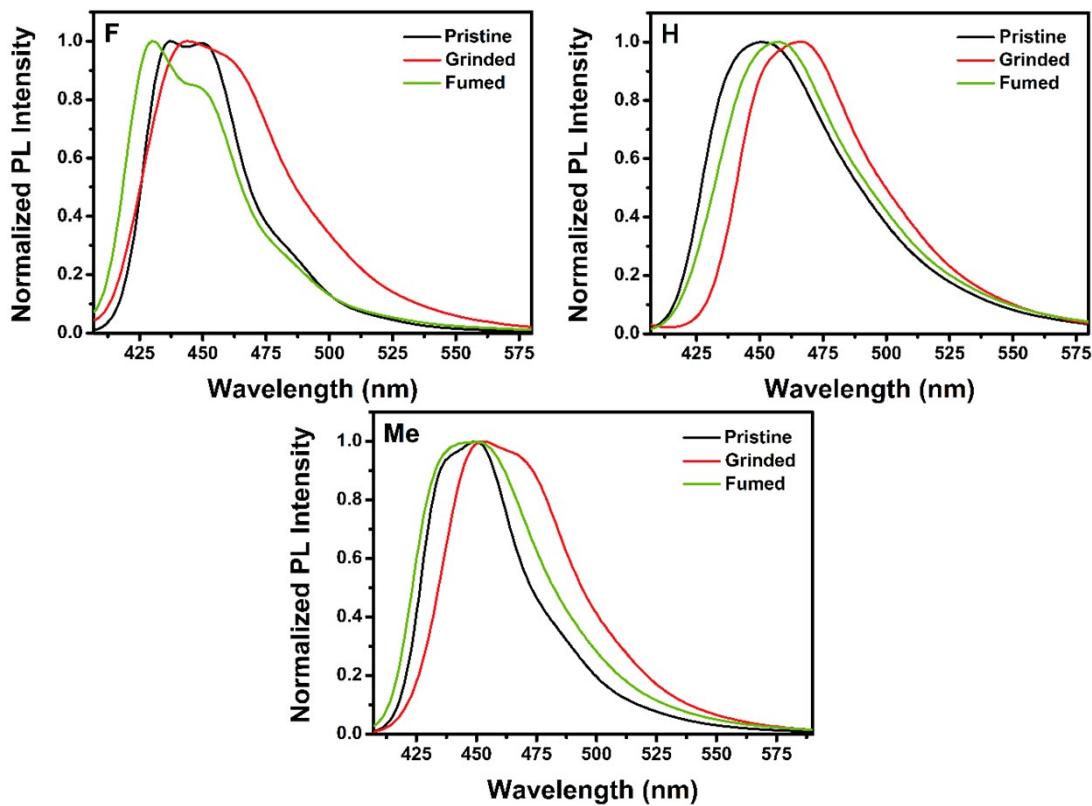
Figure S20. Emission spectra of **F**–**Me** in different solid-state: pristine, ground, and fumed powder.

Table S5. Emission peak/shoulders of **CN**–**OMe** in different solid-state

Compounds	λ_{em} (nm) pristine	λ_{em} (nm) grinding	λ_{em} (nm) acetone fuming
CN	432/446	440/456	430/448
F	437/450	444	430/448
H	450	466	458
Me	449	453	450
OMe	481	481	483
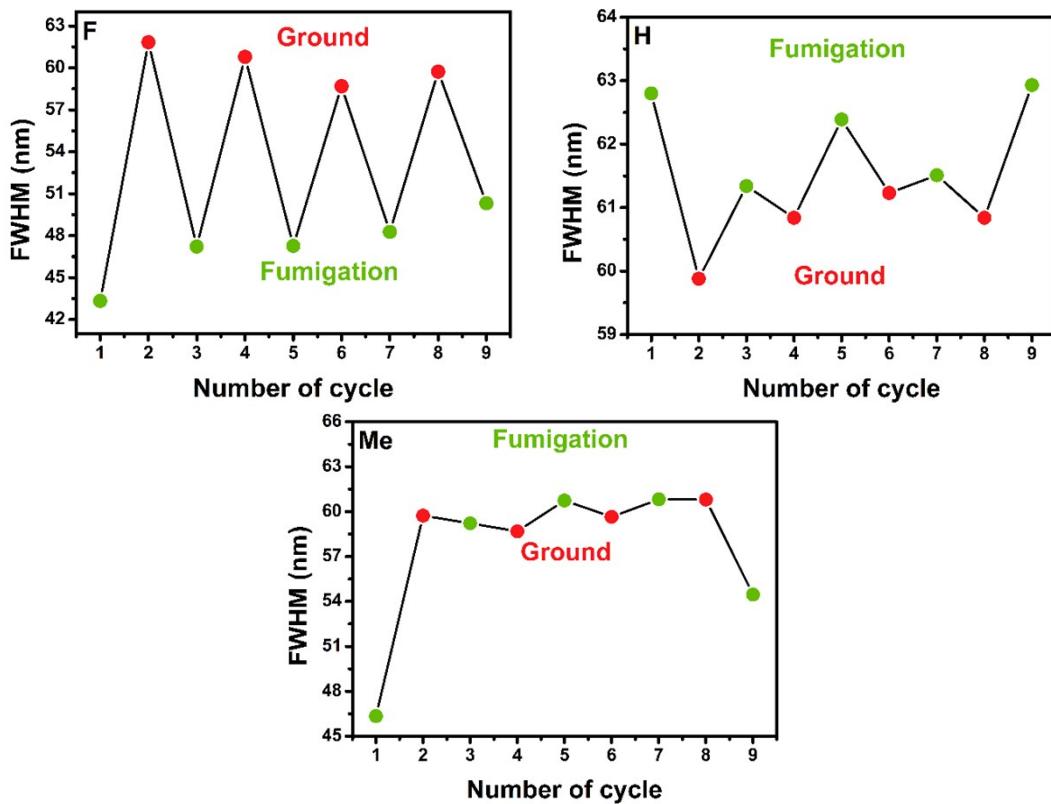
Figure S21. Reversible switching of emission of pristine powder **F–Me** by repeating grinding-acetone fuming cycles.
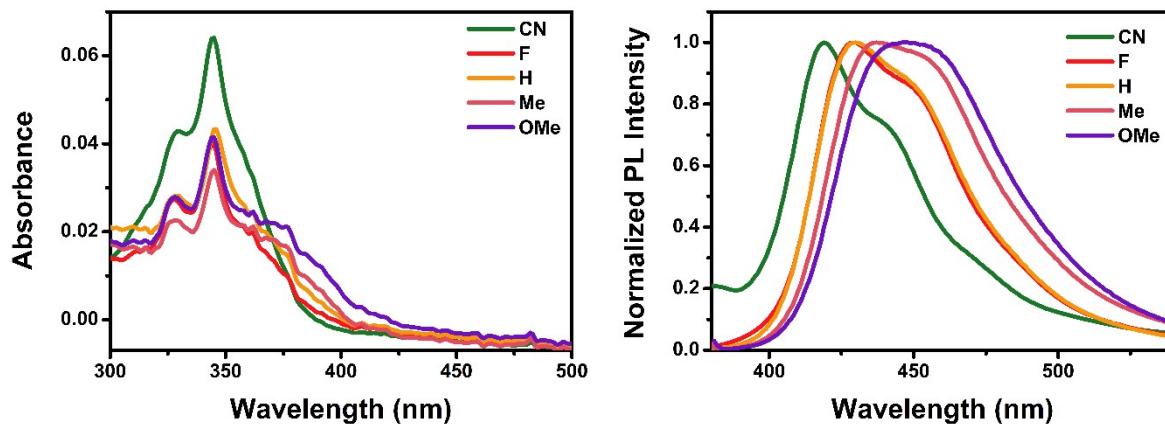
Figure S22. UV-vis absorption (left) and emission (right) spectra of **CN–OMe**, recorded at RT in PMMA film (1 wt. %).
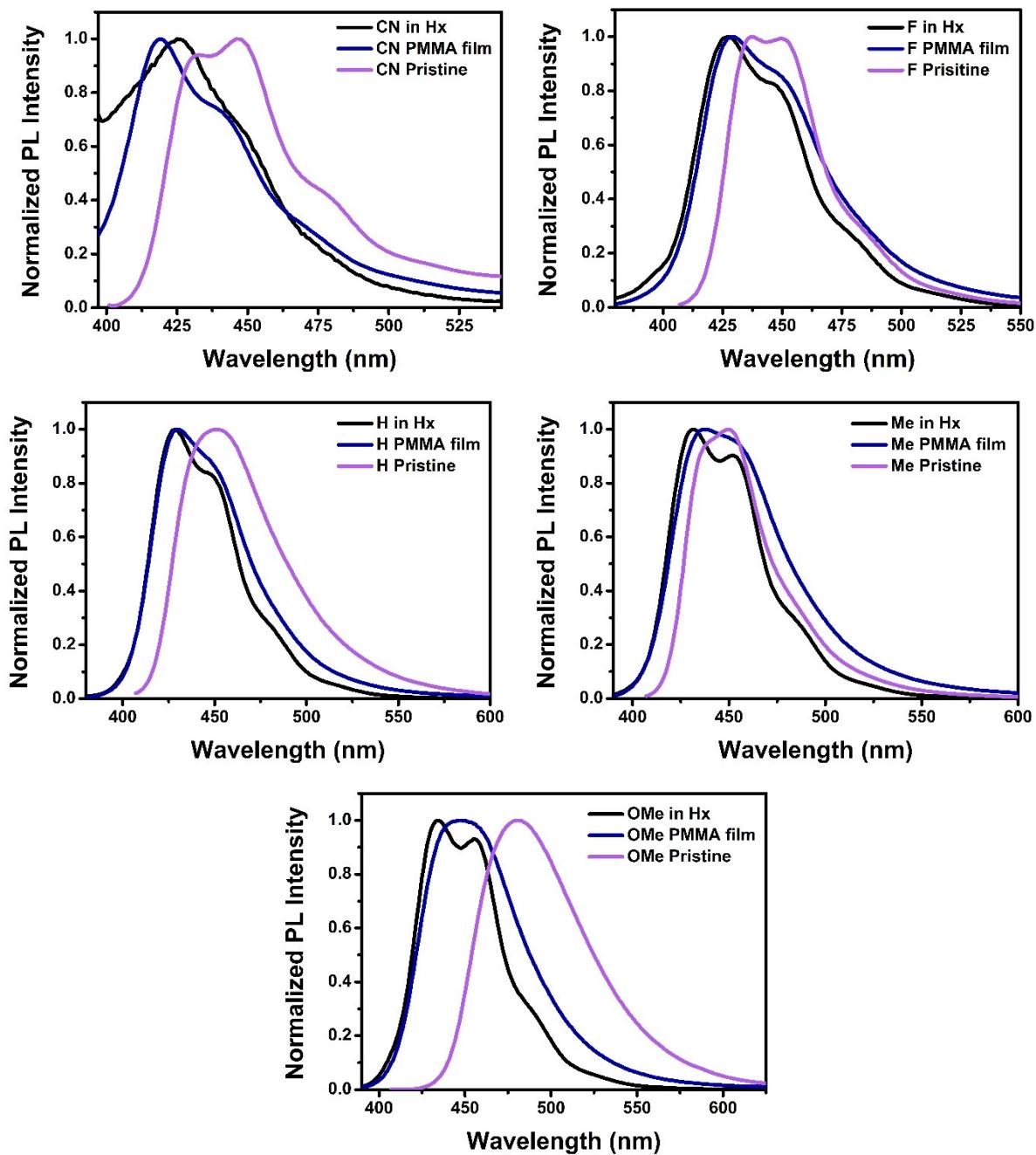
Figure S23. Comparison of emission spectra between solution and solid state for **CN–OMe**.
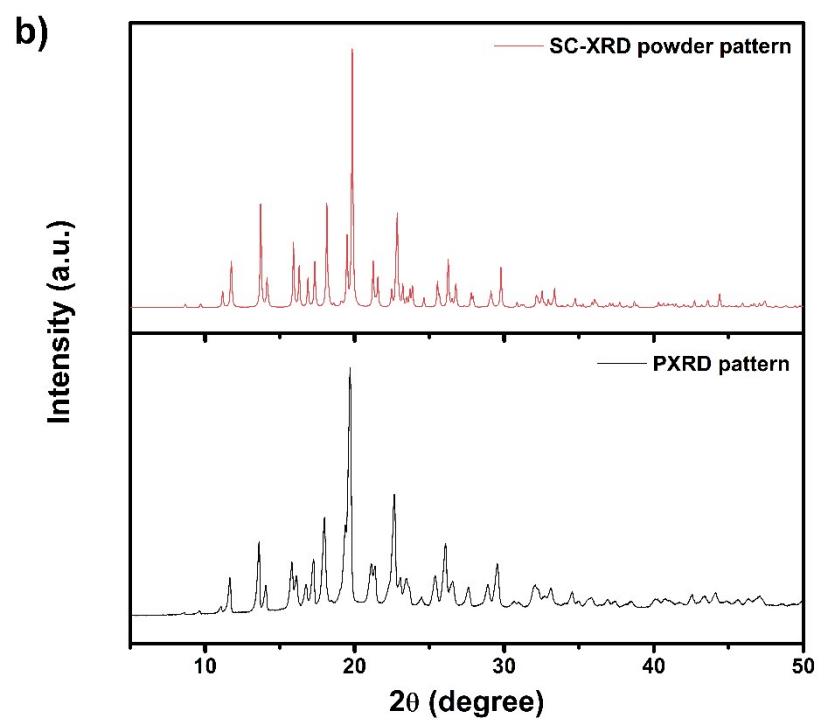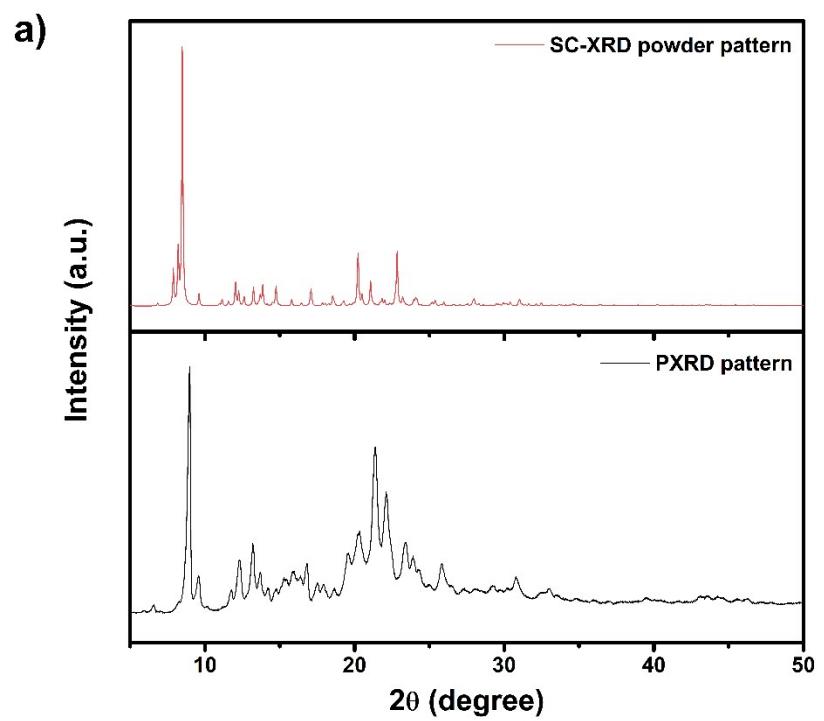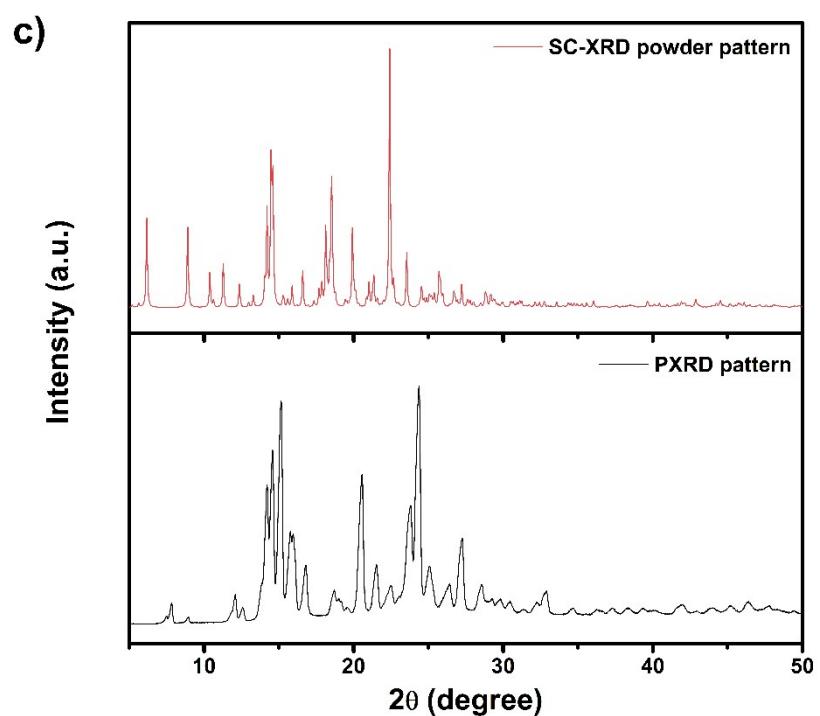
Figure S24. SC-XRD powder pattern (top) and PXRD pattern (bottom) of (a) **CN**, (b) **F**, and (c) **Me**.
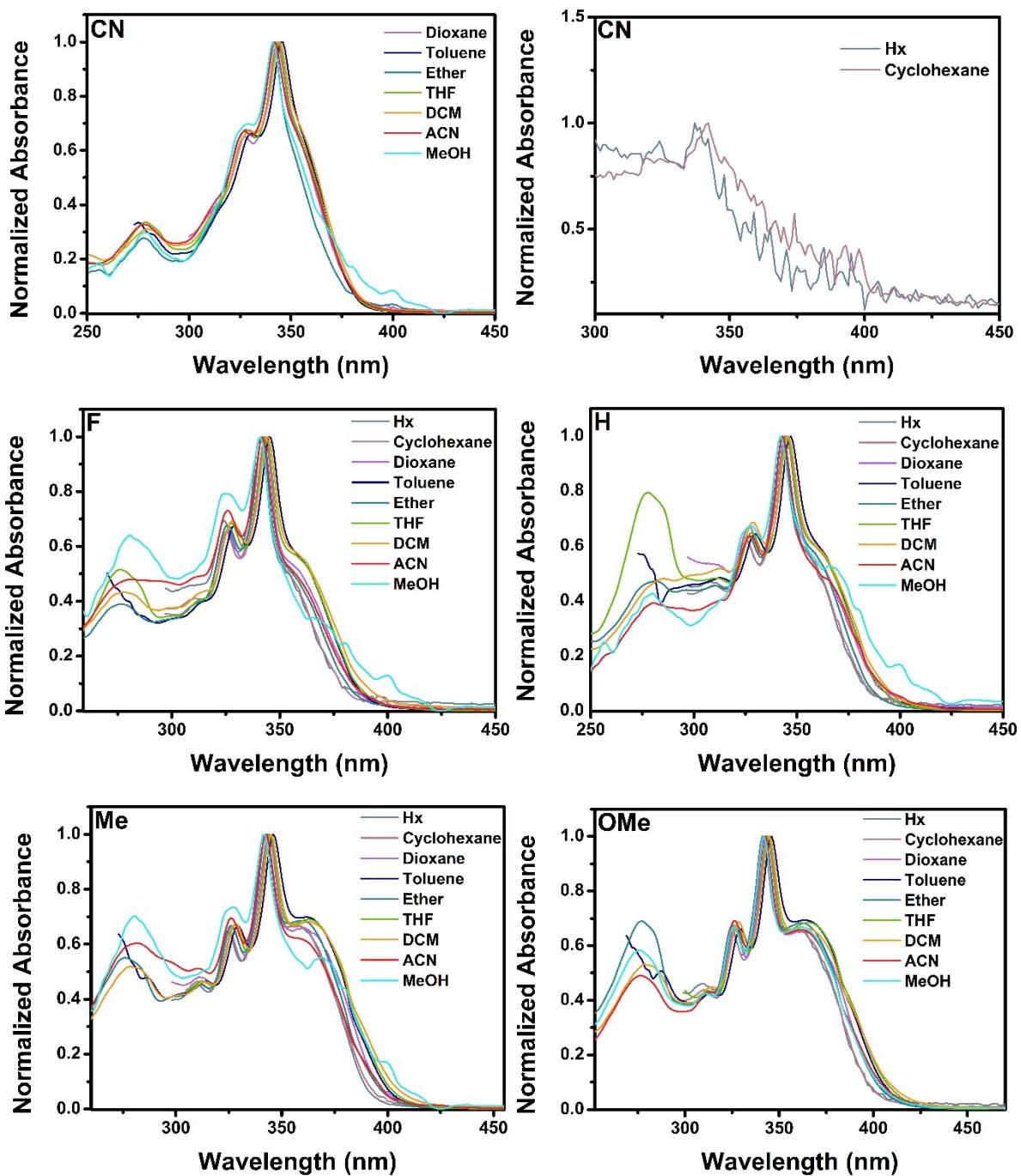
Figure S25. UV-vis absorption spectra of **CN–OMe** in various solvents at room temperature.
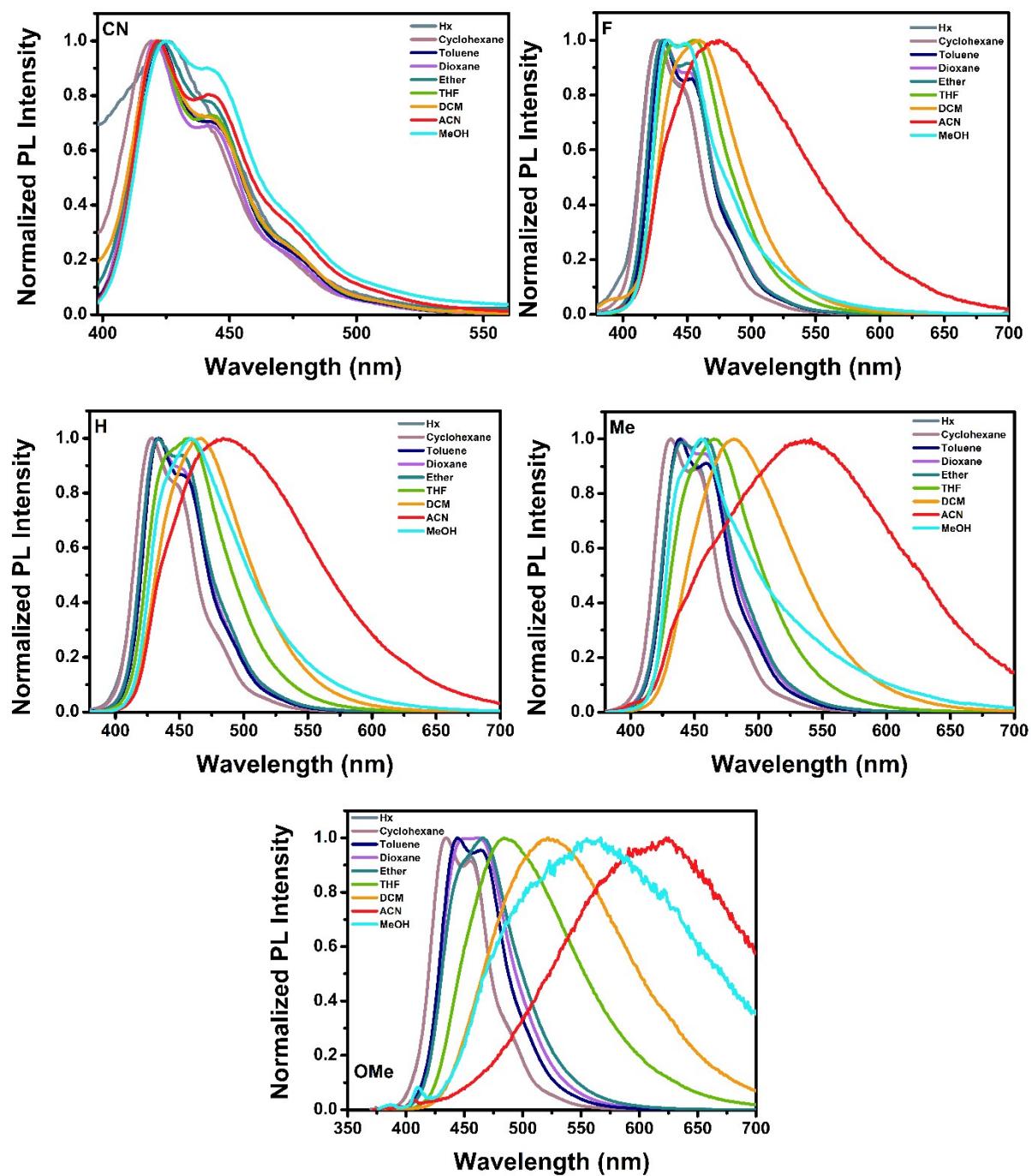
Figure S26. Emission spectra of **CN–OMe** in various solvents at room temperature.

Table S6. Spectroscopic parameters of **CN–OMe** in various solvents

compounds	Solvents	λ_{max} abs (nm)	λ_{max} em (nm)	Stokes shift (cm^{-1})
CN	*n*-Hexane	350	425	5042
	Cyclohexane	350	419	4705
	Toluene	358	422	4236
	1,4-Dioxane	352	421	4656
	Ether	352	423	4768
	THF	356	421	4337
	DCM	357	421	4258
	ACN	356	422	4393
	MeOH	352	425	4880
F	*n*-Hexane	355	428	4804
	Cyclohexane	355	427	4750
	Toluene	361	432	4553
	1,4-Dioxane	356	432	4942
	Ether	357	431	4809
	THF	360	456	5848
	DCM	360	460	6039
	ACN	359	475	6802
	MeOH	353	435	5340
H	*n*-Hexane	358	429	4623
	Cyclohexane	357	428	4647
	Toluene	364	433	4378
	1,4-Dioxane	358	433	4838
	Ether	360	433	4683
	THF	363	457	5666
	DCM	362	467	6211
	ACN	366	484	6661
	MeOH	367	459	5461
Me	*n*-Hexane	359	431	4653

	Cyclohexane	359	431	4653
	Toluene	362	439	4845
	1,4-Dioxane	360	440	5050
	Ether	359	458	6021
	THF	364	465	5967
	DCM	363	481	6758
	ACN	358	541	9449
	MeOH	369	455	5122
OMe	*n*-Hexane	360	434	4736
	Cyclohexane	360	434	4736
	Toluene	367	444	4725
	1,4-Dioxane	363	462	5903
	Ether	362	466	6165
	THF	366	484	6661
	DCM	365	522	8240
	ACN	362	623	11573
	MeOH	362	567	9988

Lippert-Mataga Calculation

The solvation effects that affect the optical properties of compounds can be understood using the Lippert-Mataga equation, a model that describes the interactions between the solvent and the dipole moment of the solute:

$$\Delta v = \bar{v}_a - \bar{v}_f = \frac{2}{hca_0^3}\left(\frac{\varepsilon - 1}{2\varepsilon + 1} + \frac{n^2 - 1}{2n^2 + 1}\right) \times (\mu_e - \mu_g)^2 + constant$$

$$= 2\Delta f \times \frac{\Delta\mu^2}{hca_0^3} + constant$$

where Δv is the Stokes shift; $\bar{v}_a$ and $\bar{v}_f$ are the absorption and emission energy in wavenumbers, respectively. $\mu_e - \mu_g$ ($\Delta\mu$) is the difference between the dipole moments of excited (μ_e) and ground (μ_g) states; c is the speed of light; h is Planck's constant, and a_0 is the radius of the Onsager cavity around the fluorophore. The solvent dielectric constant (ε) and refractive index (n) are included in the term, Δf, which is known as the solvent polarity parameter. The Onsager radii were determined by *ab initio* calculation and were considered to be half of the average molecular sizes of **CN−OMe** (27.8, 26.0, 25.6, 27.7, and 28.6 Å, respectively). As shown in Table S7, the ground state dipole moments for the energy-minimized structures (obtained by DFT) were almost zero because of the symmetry of the compounds. The excited-state dipole moments were calculated using the values of the ground state dipole moment and dipole moment change.
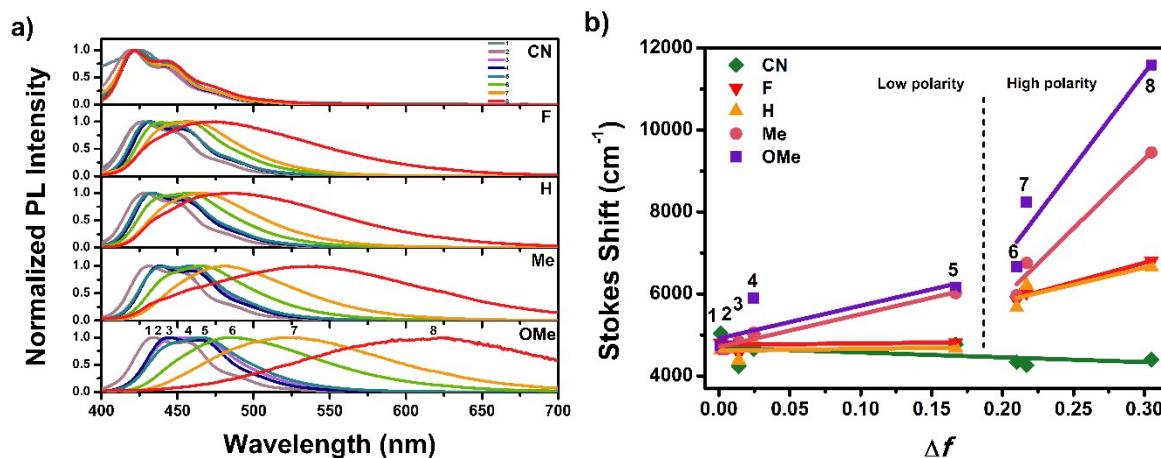
Figure S27 a) Emission spectra and b) Lippert-Mataga plots of **CN–OMe** in various solvents: 1, *n*-hexane; 2, cyclohexane; 3, toluene; 4, 1,4-dioxane; 5, ethyl ether; 6, THF; 7, CH₂Cl₂; 8, CH₃CN.
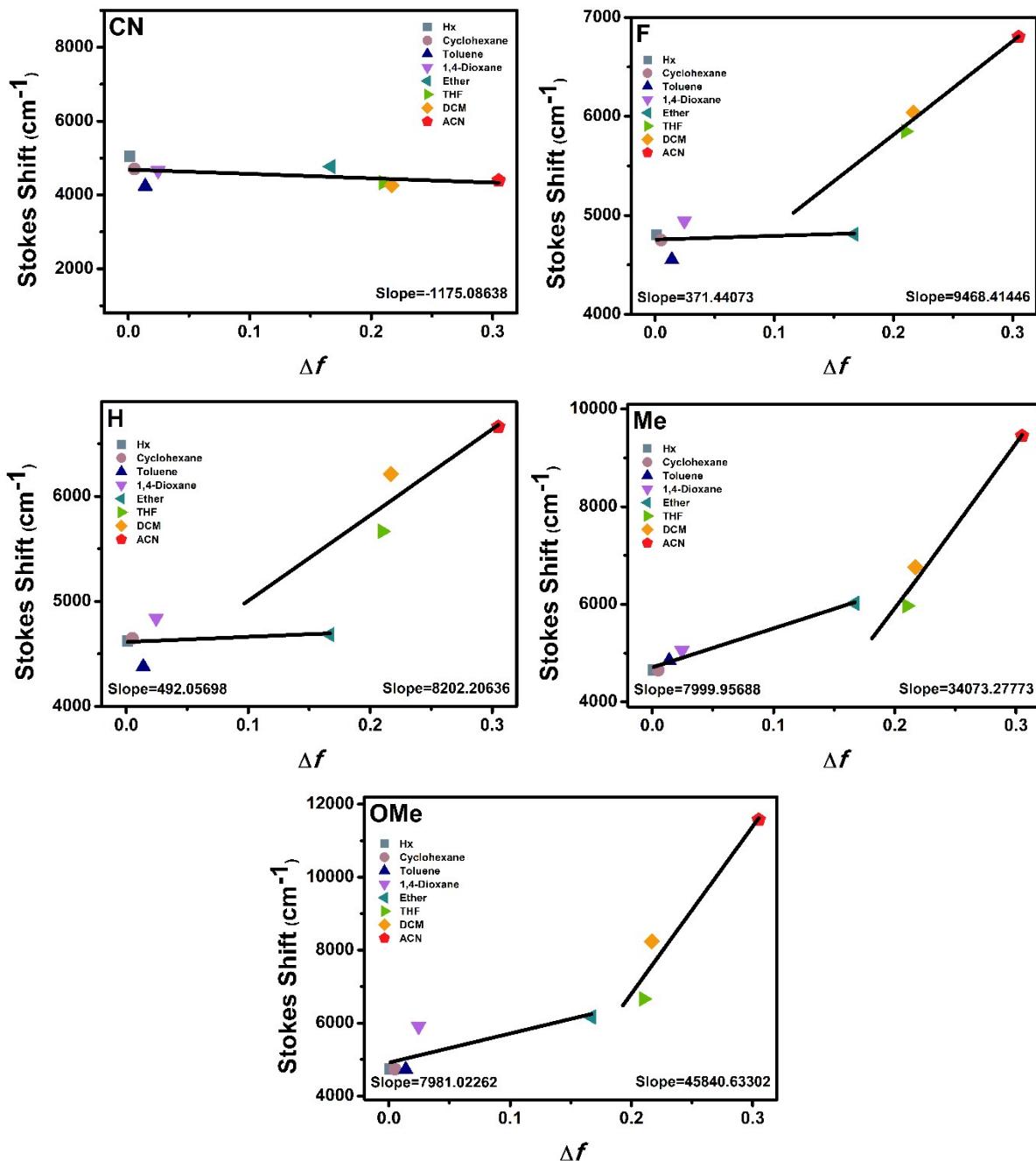
Figure S28. Lippert-Mataga plots for **CN–OMe**.

Table S7. Dipole moment values of **CN–OMe** in the ground and excited states

Compounds	$\Delta\mu$		μ_g	μ_e	
	low	high		low	high
CN	0.0 D	0.0 D	0.0004 D	0.0 D	0.0 D
F	9.0 D	45.5 D	0.0002 D	9.0 D	45.5 D
H	10.1 D	41.4 D	0.0 D	10.1 D	41.4 D
Me	46.0 D	94.8 D	0.001 D	46.0 D	94.8 D
OMe	45.2 D	108.3 D	0.0032 D	45.2 D	108.3 D
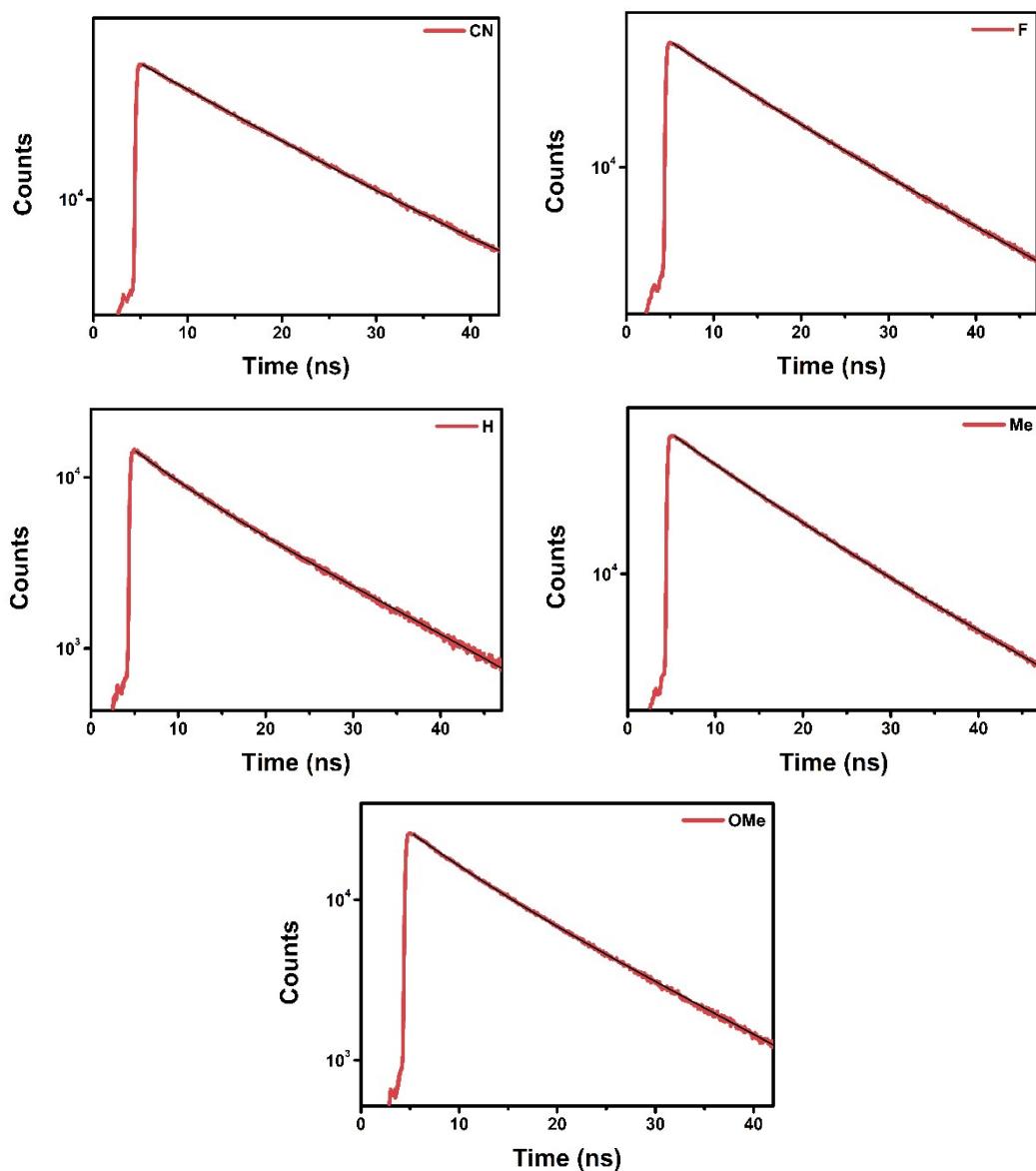
Figure S29. Fluorescence lifetimes ($^{\tau}F$) of **CN–OMe** in toluene solution at RT.
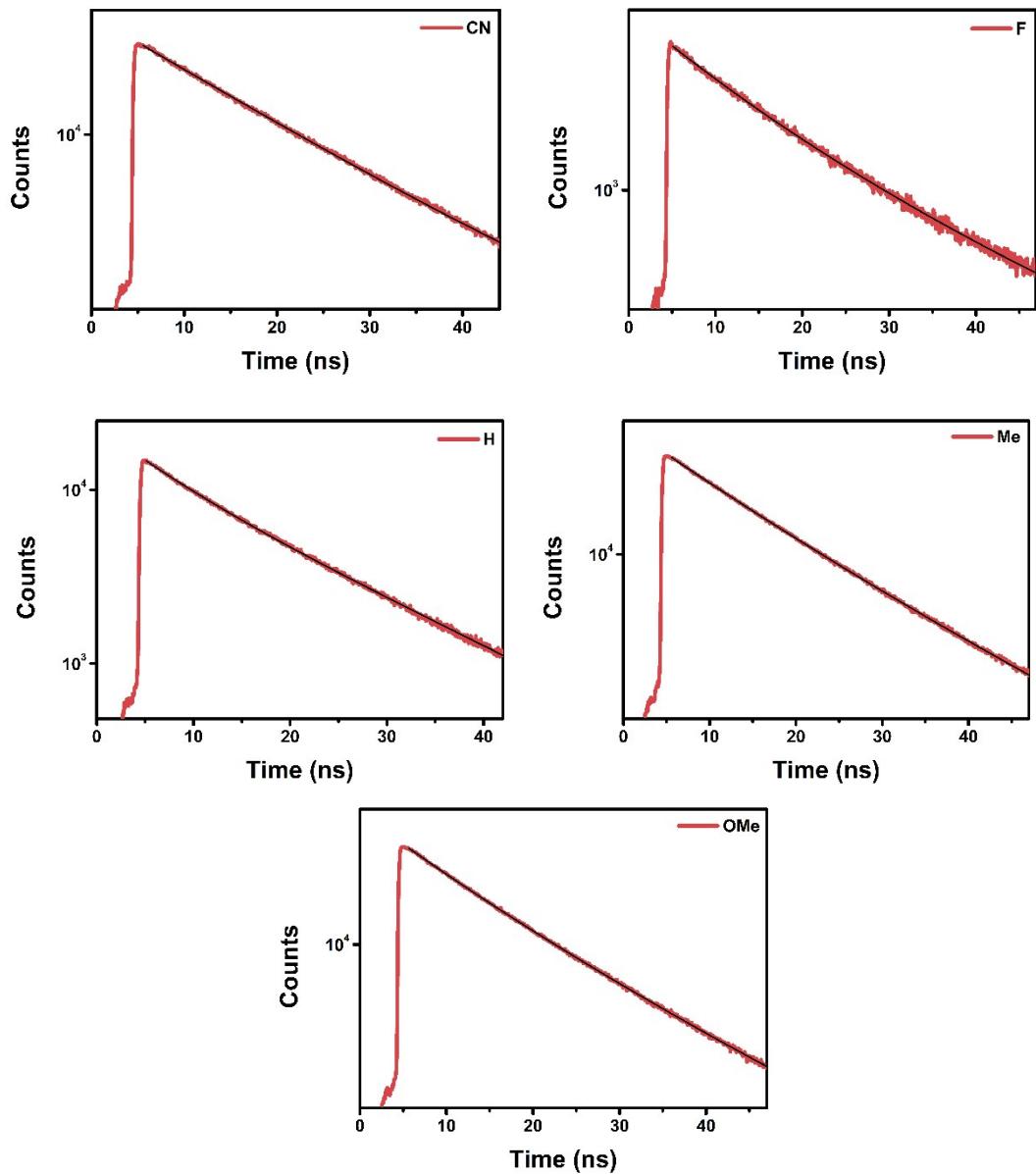
Figure S30. Fluorescence lifetimes (τ_F) of **CN–OMe** in dichloromethane solution at RT.
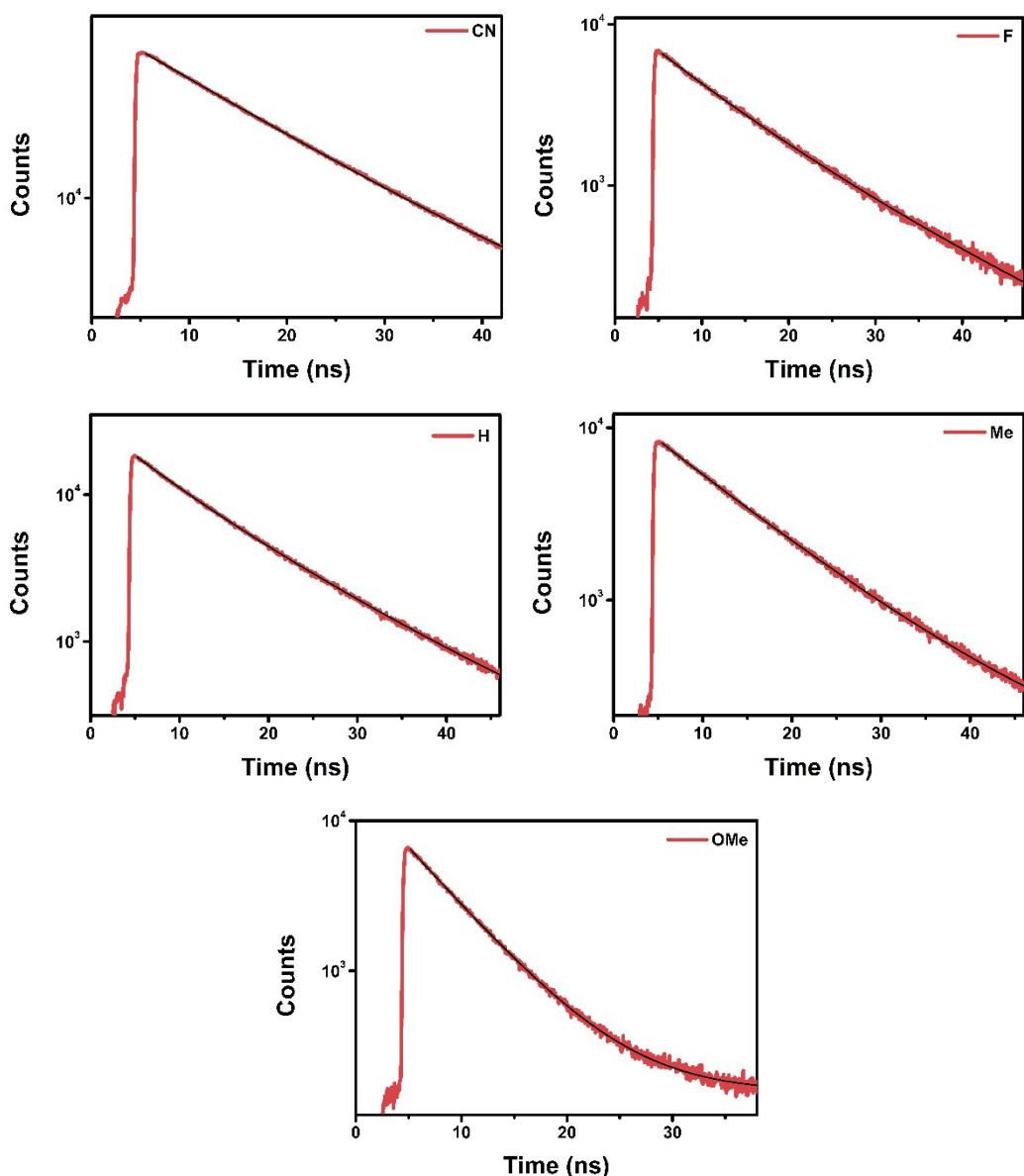
Figure S31. Fluorescence lifetimes ($^{\tau}F$) of **CN–OMe** in acetonitrile solution at RT.

Table S8. Fluorescence lifetimes ($^{\tau}F$) measured in toluene, dichloromethane, and acetonitrile.

Compounds	τ_F (ns) in toluene	τ_F (ns) in DCM	τ_F (ns) in ACN
CN	17.4	20.3	14.4
F	9.9, 17.4	8.8, 19.6	7.3, 14.3
H	7.2, 17.7	7.2, 17.8	6.5, 13.0
Me	8.8, 15.7	9.2, 15.6	9.2, 14.1

| OMe | 6.5, 14.5 | 8.6, 16.1 | 5.53 |
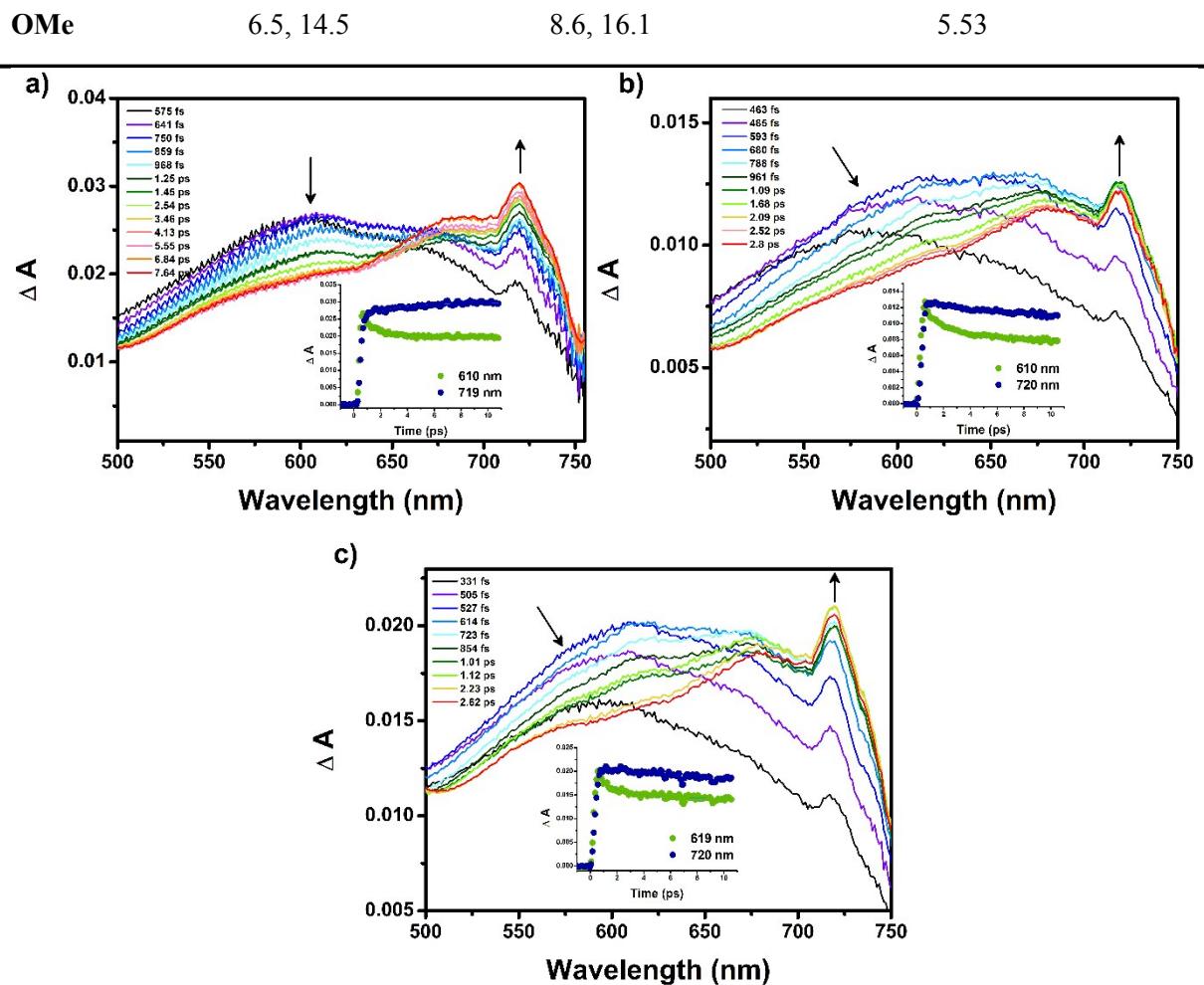
Figure S32. Chirping corrected transient absorption spectra of a) **F**, b) **H** and c) **Me** in CH₂Cl₂. The excitation wavelength was 340 nm. Inset: decay and rise profiles were monitored at selected wavelengths.
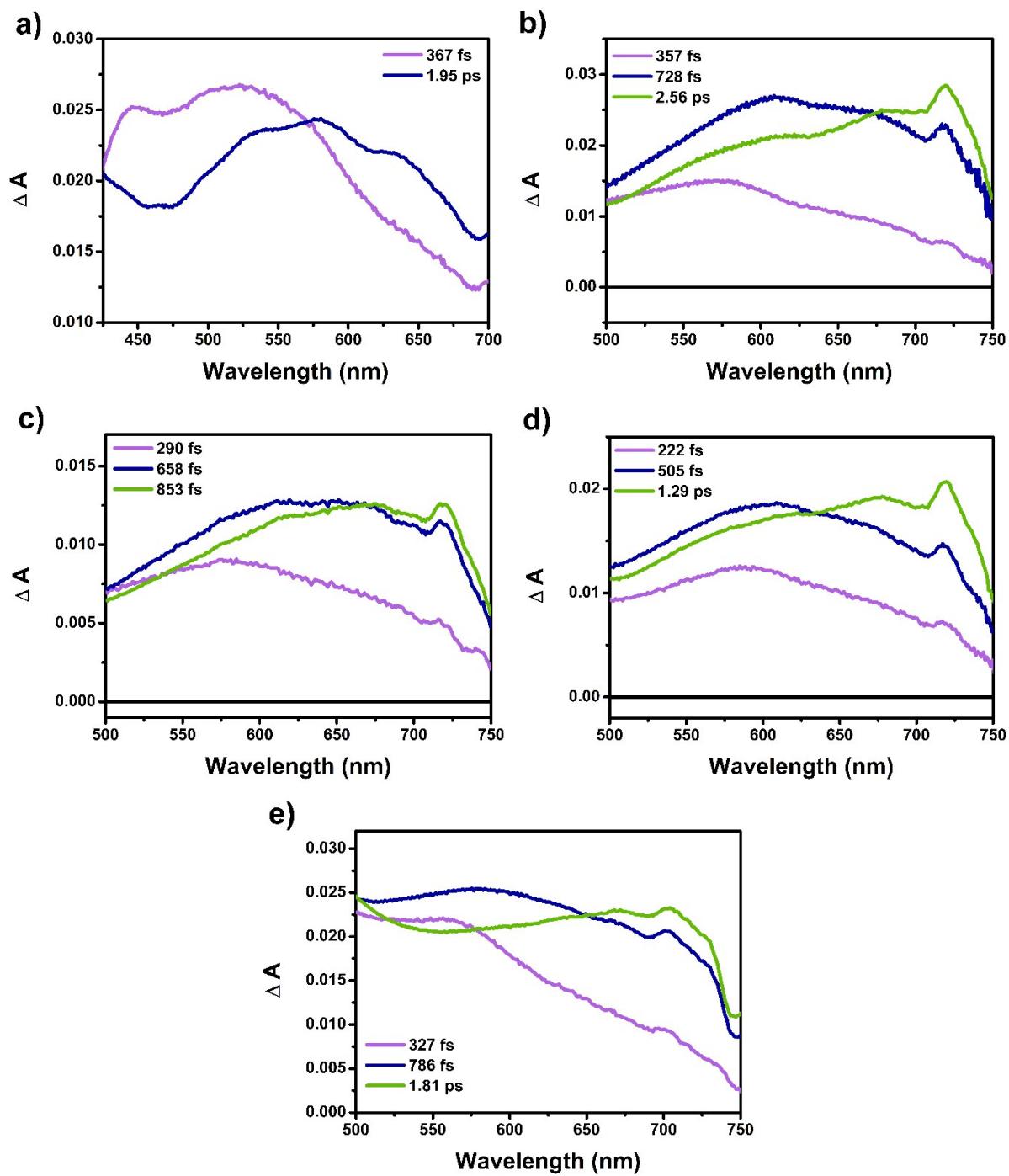
Figure S33. Chirping corrected transient absorption spectra of (a) **CN**, (b) **F**, (c) **H**, (d) **Me**, and (e) **OMe** in CH$_2$Cl$_2$. The excitation wavelength was 340 nm.

DFT/TD-DFT Calculation Details

All the calculations were performed on the platform of the Gaussian 16 package.[4] The ground-state geometry of all compounds has been optimized at the density function theory (DFT) level. Full geometry optimizations in their ground state were performed using the B3LYP functional[5-8] and the 6-31G[9, 10] basis set for all atoms. No charge and no symmetry constraints were applied during the geometry optimizations. The nature of the stationary points located was further checked by computations of harmonic vibrational frequencies at the same level of theory. As well as, all of the Cartesian coordinates for optimized structure of all compounds are also summarized in Table S10–S14. The Isodensity plots (isodensity contour = 0.04 a.u.) of the selected frontier orbitals (HOMO-3, HOMO-2, HOMO-1, HOMO, LUMO, LUMO+1, LUMO+2, LUMO+3) were visualized by Chem3D Ultra and GaussView 5.0 program (Figure S35–S39). The excitation energies and oscillator strengths for the lowest 100 singlet–singlet transitions at the optimized geometry in the ground state were obtained in TD-DFT calculations using the same basis set and functional as for the ground state. The simulated absorption spectra were obtained by the GaussSum program based on TD-DFT results (Figure S40–S44). To reduce the meaningless features, only 20 singlet–singlet transitions are summarized in Table S15–S19.

Table S9. The number of imaginary frequencies, total energies, and dipole moments for the compound **CN–OMe** as obtained in the geometry optimizations at B3LYP/6-31G method

Entry	Number of imaginary frequencies	Total energies (Eh) (Hartrees)	Ground state dipole moment (field-independent basis, Debye)
CN	0	-2481.81332514	0.0004
F	0	-2509.76571817	0.0002
H	0	-2112.84272399	0.0000
Me	0	-2270.12422887	0.0010
OMe	0	-2570.93885996	0.0032

	CN	F	H	Me	OMe
LUMO+1					
LUMO					
HOMO					
HOMO-1					
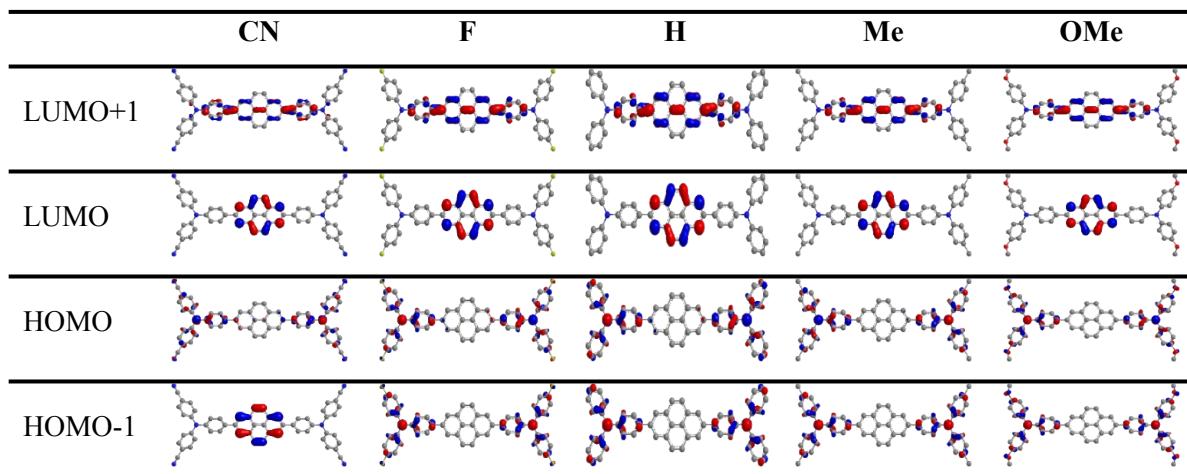
Figure S34. Frontier orbital distributions (HOMO-1, HOMO, LUMO, LUMO+1) of **CN–OMe** calculated by DFT with the B3LYP function and the 6-31G (d,p) basis.

Table S10. Cartesian coordinates for optimized structure for **CN**
Symbolic Z-matrix:
Charge = 0 Multiplicity = 1

Atom	X	Y	Z	Atom	X	Y	Z
C	-1.429336	1.23326	0.003713	C	10.146432	-3.32454	-1.426084
C	-2.830304	1.207586	0.003652	C	9.480071	-2.131299	-1.186324
C	-3.544904	-0.000024	-0.000003	C	11.172663	1.510991	-0.432744
C	-2.830311	-1.207637	-0.003662	C	11.845618	2.69881	-0.184487
C	-1.429342	-1.233319	-0.003729	C	11.3399	3.622645	0.746548
C	-0.711748	-0.000032	-0.000009	C	10.146171	3.324548	1.42609
C	0.711695	-0.000035	-0.00001	C	9.479903	2.131258	1.186314
C	1.429298	-1.233308	0.005303	C	12.029626	4.851575	0.997424
C	2.830261	-1.207633	0.005197	N	12.589618	5.851281	1.201601
C	3.544907	-0.000043	-0.000009	C	12.029991	-4.851429	-0.997373
C	2.830268	1.20755	-0.005217	N	12.59006	-5.851093	-1.201539
C	1.429304	1.233232	-0.005324	C	-12.029937	-4.851569	0.996665
C	0.680616	2.461932	-0.003011	N	-12.590006	-5.851264	1.200686
C	-0.680628	2.461942	-0.000191	C	-12.029736	4.851644	-0.99668
C	0.680601	-2.462003	0.002988	N	-12.589761	5.851363	-1.200704
C	-0.680642	-2.462005	0.000171	H	-3.370272	2.149762	-0.023273
C	5.029111	-0.000043	-0.000007	H	-3.370285	-2.14981	0.023263
C	-5.029116	-0.000022	0	H	3.370159	-2.149876	-0.020631
C	5.756806	-0.954642	0.731305	H	3.370172	2.149789	0.020609
C	7.14774	-0.954106	0.740324	H	1.228892	3.40011	-0.004577
C	7.858586	-0.000035	-0.000008	H	-1.228893	3.400128	0.00016
C	7.147734	0.954037	-0.740331	H	1.228872	-3.400185	0.00455
C	5.756799	0.954563	-0.731314	H	-1.228912	-3.400188	-0.000183
C	-5.756761	0.954578	0.731337	H	5.225704	-1.684821	1.333846
C	-7.147699	0.954038	0.740363	H	7.689204	-1.686666	1.329938
C	-7.858536	-0.000022	0.000003	H	7.689194	1.686606	-1.329938
C	-7.147702	-0.954079	-0.740361	H	5.225692	1.684742	-1.333851
C	-5.756762	-0.95462	-0.731335	H	-5.225587	1.684783	1.33379
N	9.28822	-0.000019	-0.000004	H	-7.689177	1.686573	1.329997
C	9.982293	1.206085	0.25314	H	-7.689178	-1.686613	-1.329997
C	9.982367	-1.206083	-0.253136	H	-5.22559	-1.684826	-1.333789
N	-9.288171	-0.000014	0.000002	H	-11.562672	0.815157	1.167111
C	-9.982316	-1.20612	0.252958	H	-12.759059	2.926429	0.723821
C	-9.982276	1.206113	-0.252956	H	-9.753576	4.028236	-2.151897
C	-11.172611	1.510908	0.433036	H	-8.56663	1.905734	-1.724316
C	-11.845609	2.698741	0.184962	H	-11.562684	-0.815101	-1.16712
C	-11.339967	3.622699	-0.745994	H	-12.75916	-2.926325	-0.723844
C	-10.146275	3.32471	-1.425647	H	-9.753759	-4.028251	2.151912
C	-9.479967	2.131405	-1.186054	H	-8.566724	-1.9058	1.724344
C	-11.172657	-1.510868	-0.433042	H	11.562809	-0.815218	1.166905
C	-11.845707	-2.698674	-0.184975	H	12.75928	-2.926373	0.723321
C	-11.340114	-3.622653	0.745985	H	9.753739	-4.028001	-2.152401
C	-10.146419	-3.324711	1.425654	H	8.566708	-1.905617	-1.72453
C	-9.480059	-2.131434	1.186067	H	11.562784	0.815342	-1.166883
C	11.172749	-1.510901	0.432764	H	12.759095	2.926582	-0.723265
C	11.845796	-2.698672	0.184526	H	9.753407	4.027979	2.152398
C	11.340166	-3.62255	-0.746514	H	8.566538	1.905505	1.724494

Table S11. Cartesian coordinates for optimized structure for **F**
Symbolic Z-matrix:
Charge = 0 Multiplicity = 1

Atom	X	Y	Z	Atom	X	Y	Z
C	1.430267	-1.232711	0.003998	C	-11.835153	2.609707	0.801338
C	2.831175	-1.206747	0.002287	C	-11.423802	3.626033	-0.052866
C	3.548371	0.000003	0.000001	C	-10.323894	3.474734	-0.889354
C	2.831176	1.206753	-0.002284	C	-9.625688	2.269563	-0.8763
C	1.430268	1.232718	-0.003994	C	-11.117969	-1.415731	-0.825191
C	0.711696	0.000004	0.000002	C	-11.835127	-2.609727	-0.801341
C	-0.711677	0.000004	0.000002	C	-11.423765	-3.626049	0.052863
C	-1.430252	1.232713	0.004593	C	-10.323858	-3.474739	0.889351
C	-2.831159	1.20675	0.002868	C	-9.625665	-2.26956	0.876297
C	-3.548367	0.000005	0.000002	F	-12.110027	4.78925	-0.071246
C	-2.83116	-1.20674	-0.002863	F	-12.109978	-4.789273	0.071242
C	-1.430253	-1.232704	-0.004589	F	12.109995	-4.789266	-0.070895
C	-0.680692	-2.461069	-0.001826	F	12.110007	4.78926	0.070891
C	0.680703	-2.461072	0.000643	H	3.370916	-2.149063	-0.02646
C	-0.680691	2.461078	0.001831	H	3.370917	2.149069	0.026463
C	0.680704	2.461079	-0.000638	H	-3.37088	2.149088	-0.025469
C	-5.031527	0.000005	0.000002	H	-3.370881	-2.149079	0.025473
C	5.031532	0.000002	0.000001	H	-1.229092	-3.399366	-0.00283
C	-5.76335	0.964696	0.713404	H	1.2291	-3.399369	0.001196
C	-7.153395	0.964991	0.723665	H	-1.22909	3.399374	0.002836
C	-7.873834	0.000005	0.000001	H	1.229102	3.399377	-0.001192
C	-7.153394	-0.964981	-0.723662	H	-5.234619	1.705316	1.305895
C	-5.763349	-0.964686	-0.7134	H	-7.689272	1.708054	1.304316
C	5.763342	-0.964648	0.713465	H	-7.689272	-1.708045	-1.304312
C	7.153389	-0.964939	0.723728	H	-5.234619	-1.705307	-1.30589
C	7.873824	0.000001	0	H	5.234592	-1.705249	1.305963
C	7.153389	0.964942	-0.723729	H	7.689271	-1.707961	1.304428
C	5.763343	0.964652	-0.713464	H	7.689271	1.707964	-1.304428
N	-9.291106	0.000002	0	H	5.234593	1.705254	-1.305962
C	-10.008987	-1.228383	0.015365	H	11.418582	-0.618942	1.497
C	-10.008998	1.228381	-0.015367	H	12.693919	-2.764477	1.445479
N	9.291098	0	-0.000001	H	10.036101	-4.285952	-1.548968
C	10.008987	1.228382	0.015275	H	8.774571	-2.131611	-1.534038
C	10.008984	-1.228383	-0.015277	H	11.418583	0.618938	-1.497003
C	11.117959	-1.415669	0.825303	H	12.693926	2.764469	-1.445482
C	11.835123	-2.609663	0.80154	H	10.036113	4.285951	1.548966
C	11.423776	-3.626045	-0.0526	H	8.774577	2.131613	1.534037
C	10.323876	-3.474796	-0.889109	H	-11.418609	0.619035	1.496936
C	9.625677	-2.26962	-0.876143	H	-12.693957	2.764559	1.445257
C	11.117962	1.415665	-0.825305	H	-10.036116	4.285847	-1.549265
C	11.835129	2.609658	-0.801543	H	-8.774575	2.131514	-1.534177
C	11.423785	3.62604	0.052597	H	-11.418603	-0.61905	-1.496939
C	10.323886	3.474795	0.889107	H	-12.693929	-2.764588	-1.445261
C	9.625683	2.26962	0.876142	H	-10.036072	-4.285849	1.549261
C	-11.117983	1.415718	0.825188	H	-8.774553	-2.131502	1.534174

Table S12. Cartesian coordinates for optimized structure for **H**
Symbolic Z-matrix:
Charge = 0 Multiplicity = 1

Atom	X	Y	Z	Atom	X	Y	Z
C	1.430377	-1.232658	0.004261	C	-11.838739	2.631675	0.695166
C	2.831295	-1.206663	0.002479	C	-11.421397	3.65659	-0.156201
C	3.548708	-0.000001	-0.00001	C	-10.29319	3.462255	-0.955549
C	2.831295	1.206662	-0.002502	C	-9.593795	2.257913	-0.914439
C	1.430378	1.232658	-0.004288	C	-11.135277	-1.430595	-0.757101
C	0.711692	0	-0.000014	C	-11.838736	-2.631681	-0.695141
C	-0.711692	0	-0.000014	C	-11.421386	-3.656595	0.156223
C	-1.430377	1.232658	0.004267	C	-10.293174	-3.462257	0.955563
C	-2.831294	1.206664	0.002485	C	-9.593783	-2.257913	0.914449
C	-3.548708	0.000001	-0.00001	H	3.371128	-2.148928	-0.026065
C	-2.831295	-1.206662	-0.002507	H	3.371129	2.148927	0.026044
C	-1.430378	-1.232657	-0.004294	H	-3.371128	2.148929	-0.026055
C	-0.680711	-2.460972	-0.001242	H	-3.371129	-2.148927	0.026034
C	0.68071	-2.460973	0.001201	H	-1.229161	-3.399266	-0.002027
C	-0.68071	2.460973	0.001212	H	1.22916	-3.399266	0.001978
C	0.680711	2.460973	-0.001231	H	-1.22916	3.399267	0.001995
C	-5.031918	0.000001	-0.000006	H	1.229161	3.399266	-0.002011
C	5.031918	-0.000001	-0.000006	H	-5.234409	1.706406	1.304703
C	-5.763413	0.965477	0.712789	H	-7.690558	1.709163	1.301626
C	-7.153463	0.965487	0.722884	H	-7.690565	-1.70916	-1.301624
C	-7.87353	0.000001	0.000001	H	-5.234416	-1.706403	-1.304714
C	-7.153467	-0.965484	-0.722885	H	5.234409	-1.706404	1.304705
C	-5.763417	-0.965475	-0.712798	H	7.690558	-1.709161	1.301628
C	5.763413	-0.965476	0.71279	H	7.690565	1.709159	-1.301626
C	7.153463	-0.965486	0.722885	H	5.234416	1.706402	-1.304716
C	7.87353	-0.000001	0.000001	H	11.455497	-0.642184	1.429896
C	7.153467	0.965484	-0.722886	H	12.710539	-2.770481	1.328178
C	5.763416	0.965475	-0.712799	H	11.967954	-4.593678	-0.196439
N	-9.291493	0.000001	0.000005	H	9.960909	-4.247292	-1.628845
C	-10.005573	-1.229261	0.05195	H	8.726361	-2.106392	-1.547979
C	-10.005576	1.229261	-0.051936	H	11.455505	0.642187	-1.429873
N	9.291493	0	0.000005	H	12.710542	2.770486	-1.328148
C	10.005573	1.229261	0.051949	H	11.967944	4.593682	0.196464
C	10.005576	-1.229261	-0.051935	H	9.960891	4.247293	1.628857
C	11.135275	-1.430591	0.757123	H	8.726347	2.10639	1.547985
C	11.838738	-2.631675	0.695169	H	-11.455497	0.642185	1.429895
C	11.421395	-3.656591	-0.156197	H	-12.71054	2.770481	1.328175
C	10.293188	-3.462257	-0.955544	H	-11.967956	4.593677	-0.196444
C	9.593794	-2.257914	-0.914436	H	-9.960911	4.24729	-1.62885
C	11.135277	1.430594	-0.757103	H	-8.726362	2.10639	-1.547982
C	11.838737	2.631679	-0.695144	H	-11.455505	-0.642189	-1.429872
C	11.421387	3.656594	0.156219	H	-12.710541	-2.770489	-1.328144
C	10.293176	3.462258	0.955559	H	-11.967941	-4.593683	0.196469
C	9.593784	2.257914	0.914447	H	-9.960888	-4.247291	1.628862
C	-11.135276	1.430592	0.757122	H	-8.726345	-2.106388	1.547986

Table S13. Cartesian coordinates for optimized structure for **Me**
Symbolic Z-matrix:
Charge = 0 Multiplicity = 1

Atom	X	Y	Z	Atom	X	Y	Z
C	1.43055	-1.232571	0.00426	C	-11.447683	-3.672746	0.054922
C	2.831451	-1.206533	0.002228	C	-10.322415	-3.479451	0.866882
C	3.549293	0.000008	0.000043	C	-9.617836	-2.278306	0.862501
C	2.831451	1.206549	-0.002147	C	-12.232024	4.962545	-0.096782
C	1.43055	1.232587	-0.004188	C	-12.23196	-4.962578	0.096751
C	0.711694	0.000008	0.000033	C	12.231893	-4.962629	-0.096817
C	-0.711652	0.000008	0.000027	C	12.231932	4.962619	0.096649
C	-1.430511	1.232584	0.004341	H	3.371228	-2.14883	-0.026722
C	-2.831411	1.206546	0.00229	H	3.371228	2.148846	0.026807
C	-3.549262	0.000008	0.000013	H	-3.371176	2.14885	-0.026625
C	-2.831411	-1.206531	-0.002257	H	-3.371176	-2.148835	0.026652
C	-1.43051	-1.232569	-0.004293	H	-1.229153	-3.399148	-0.002105
C	-0.680705	-2.460823	-0.001283	H	1.22919	-3.39915	0.001903
C	0.680744	-2.460824	0.001153	H	-1.229153	3.399164	0.002157
C	-0.680706	2.460838	0.001338	H	1.22919	3.399166	-0.00183
C	0.680743	2.460839	-0.001087	H	-5.235848	1.710516	1.299113
C	-5.032243	0.000007	0.000005	H	-7.690655	1.713829	1.295839
C	5.032276	0.000008	0.000047	H	-7.690639	-1.713818	-1.295858
C	-5.764468	0.967556	0.709292	H	-5.235832	-1.710504	-1.299105
C	-7.154347	0.967994	0.719307	H	5.235846	-1.710265	1.299466
C	-7.875876	0.000006	-0.000012	H	7.690675	-1.713554	1.296243
C	-7.154338	-0.967982	-0.719322	H	7.690681	1.713572	-1.296136
C	-5.764459	-0.967542	-0.70929	H	5.235852	1.710281	-1.29937
C	5.764485	-0.967408	0.709529	H	11.437829	-0.616506	1.47395
C	7.154365	-0.967839	0.719559	H	12.695239	-2.736366	1.43116
C	7.875895	0.000008	0.000053	H	9.996357	-4.279278	-1.527455
C	7.154368	0.967856	-0.719455	H	8.756533	-2.149781	-1.509674
C	5.764488	0.967424	-0.70943	H	11.437982	0.616311	-1.473724
N	-9.291862	0.000002	-0.000021	H	12.695421	2.736155	-1.431044
C	-10.009639	-1.228755	0.018054	H	9.996271	4.279444	1.527128
C	-10.009654	1.228749	-0.018091	H	8.756427	2.149974	1.509476
N	9.291883	0.000005	0.00006	H	-11.437771	0.616434	1.473954
C	10.009663	1.228756	0.018075	H	-12.69526	2.736251	1.431206
C	10.009645	-1.228764	-0.018059	H	-9.996523	4.279268	-1.527485
C	11.127857	-1.415294	0.808401	H	-8.756625	2.149817	-1.50975
C	11.833736	-2.615085	0.778848	H	-11.437741	-0.616474	-1.47402
C	11.447632	-3.672788	-0.054975	H	-12.695203	-2.736309	-1.431268
C	10.322334	-3.479474	-0.86688	H	-9.996488	-4.279257	1.52748
C	9.617779	-2.27831	-0.862475	H	-8.756618	-2.149789	1.50974
C	11.127951	1.415174	-0.808293	H	-12.702742	5.176204	0.867773
C	11.833849	2.614966	-0.778808	H	-11.592845	5.812139	-0.355439
C	11.447687	3.672766	0.054845	H	-13.033359	4.920064	-0.845577
C	10.322301	3.479561	0.866673	H	-12.702592	-5.176296	-0.867832
C	9.617733	2.278417	0.862339	H	-11.592789	-5.812149	0.355507
C	-11.127845	1.415236	0.8084	H	-13.03336	-4.92007	0.845475
C	-11.83377	2.615005	0.778873	H	12.701835	-5.176796	0.868007
C	-11.447731	3.672722	-0.054953	H	11.592876	-5.812058	-0.356408
C	-10.322449	3.479451	-0.8669	H	13.033836	-4.919809	-0.844942
C	-9.617853	2.278316	-0.862521	H	12.703791	5.175557	-0.867503
C	-11.127815	-1.415266	-0.808452	H	11.592449	5.812413	0.353916
C	-11.833724	-2.615043	-0.778923	H	13.032366	4.920702	0.84644

Table S14. Cartesian coordinates for optimized structure for **OMe**
Symbolic Z-matrix:
Charge = 0 Multiplicity = 1

| Atom	X	Y	Z	Atom	X	Y	Z
C	2.831564	-1.206312	0.001209	C	-9.678886	2.298024	-0.78369
C	1.43071	-1.232417	0.003814	O	-12.238512	4.762543	0.259753
C	0.711577	0.000002	0.000032	O	-12.238546	-4.762528	-0.259793
C	1.430708	1.232422	-0.003744	O	12.238613	-4.762364	0.260123
C	2.831562	1.206319	-0.00113	O	12.238739	4.762292	-0.260219
C	3.550225	0.000004	0.000043	C	11.925928	5.876862	0.558567
C	-0.711703	0.000001	0.000025	C	11.925892	-5.876828	-0.558842
C	-1.430835	-1.232415	-0.004402	C	-11.925485	-5.877126	0.55886
C	-2.831685	-1.206314	-0.001788	C	-11.925393	5.877158	-0.558854
C	-3.550358	-0.000001	0.000009	H	3.371052	-2.148752	-0.028858
C	-2.831686	1.206314	0.001816	H	3.371049	2.14876	0.028939
C	-1.430837	1.232416	0.004445	H	-3.37117	-2.148773	0.027723
C	0.680679	-2.460592	0.000467	H	-3.371173	2.148772	-0.027699
C	-0.680803	-2.460591	-0.001709	H	1.22911	-3.398975	0.00089
C	0.680675	2.460596	-0.000402	H	-1.229236	-3.398973	-0.002663
C	-0.680807	2.460594	0.001761	H	1.229105	3.39898	-0.000818
C	5.0328	0.000006	0.000047	H	-1.229241	3.398975	0.002711
C	-5.032925	-0.000002	0.000002	H	-5.23887	1.72001	1.286104
C	-5.766629	0.972343	0.701293	H	-7.690744	1.724944	1.282134
C	-7.156214	0.973974	0.710899	H	-7.690727	-1.724949	-1.282164
C	-7.880464	-0.000004	-0.000013	H	-5.238853	-1.72001	-1.286108
C	-7.156205	-0.97398	-0.710921	H	5.238735	-1.72063	1.28531
C	-5.766619	-0.972346	-0.701299	H	7.690589	-1.725615	1.281305
C	5.766493	-0.97269	0.700846	H	7.690591	1.72564	-1.281189
C	7.156082	-0.97434	0.710455	H	5.238737	1.720645	-1.285209
C	7.880346	0.000011	0.000057	H	11.379271	-0.55676	1.581054
C	7.156084	0.974361	-0.710344	H	12.665672	-2.684333	1.641695
C	5.766495	0.972705	-0.700745	H	10.09207	-4.310581	-1.392796
N	-9.292866	-0.000002	-0.00002	H	8.848649	-2.193881	-1.474311
C	-10.018048	-1.225758	-0.048738	H	11.379486	0.556543	-1.580743
C	-10.01804	1.225758	0.048701	H	12.665933	2.684076	-1.641477
N	9.29274	0.000009	0.000063	H	10.091971	4.310752	1.392478
C	10.017982	1.225726	-0.048805	H	8.848503	2.194091	1.4741
C	10.017957	-1.225734	0.04886	H	-11.379971	-0.556655	-1.580348
C	11.103618	-1.378678	0.928641	H	-12.666231	-2.684291	-1.640858
C	11.825827	-2.562746	0.965595	H	-10.091408	-4.31085	1.392426
C	11.470787	-3.637877	0.137924	H	-8.848127	-2.194089	1.47385
C	10.386422	-3.500906	-0.73578	H	-11.380029	0.556632	1.580243
C	9.679225	-2.297861	-0.783879	H	-12.666271	2.684277	1.640753
C	11.103761	1.378543	-0.928464	H	-10.091314	4.310886	-1.39239
C	11.825998	2.562593	-0.96547	H	-8.848049	2.194117	-1.473817
C	11.470875	3.637835	-0.13798	H	12.648975	6.652536	0.302053
C	10.386393	3.500991	0.735599	H	10.912269	6.251477	0.365107
C	9.679166	2.297967	0.783757	H	12.019545	5.636301	1.625581
C	-11.104019	-1.378645	-0.928154	H	12.648895	-6.652544	-0.30233
C	-11.826153	-2.56276	-0.965036	H	10.912203	-6.251452	-0.365559
C	-11.470743	-3.638008	-0.137676	H	12.019651	-5.636135	-1.625813
C	-10.386068	-3.501094	0.73565	H	-12.648542	-6.652831	0.302467
C	-9.678937	-2.298006	0.783693	H	-10.911848	-6.25167	0.365153
C	-11.104043	1.378634	0.928078	H	-12.018878	-5.63663	1.625908
C	-11.826168	2.562755	0.96496	H	-12.648446	6.652872	-0.302469
C	-11.470716	3.638019	0.137641	H	-10.911756	6.251676	-0.365093
C	-10.386007	3.501117	-0.735645	H	-12.018746	5.636697	-1.625914
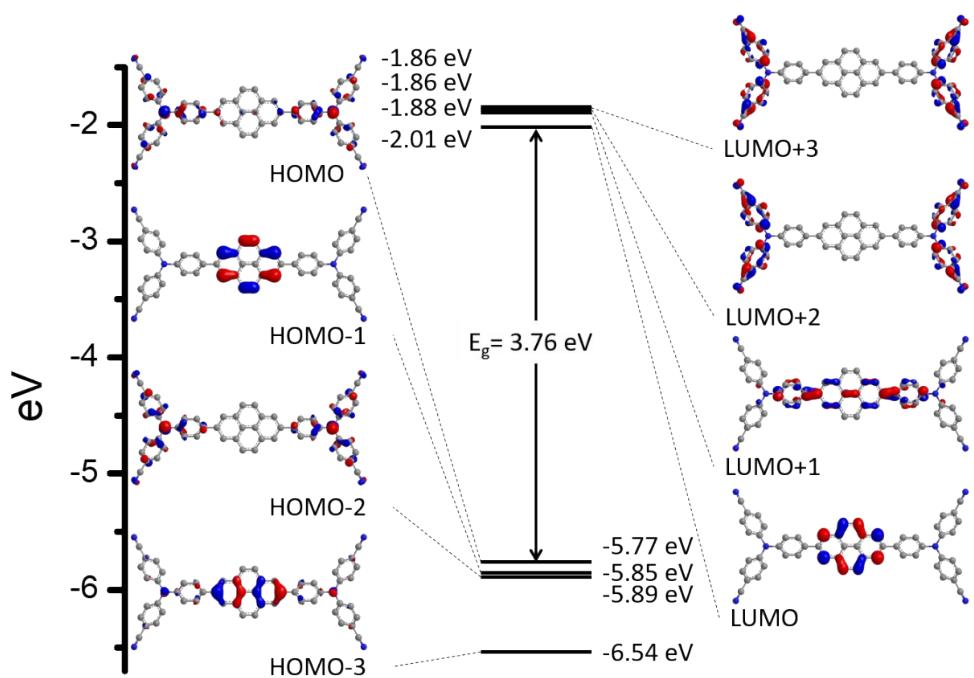
Figure S35. Energy levels and isodensity plots (isodensity contour = 0.04 a.u.) for selected occupied and unoccupied molecular orbitals of **CN** obtained by DFT calculations.
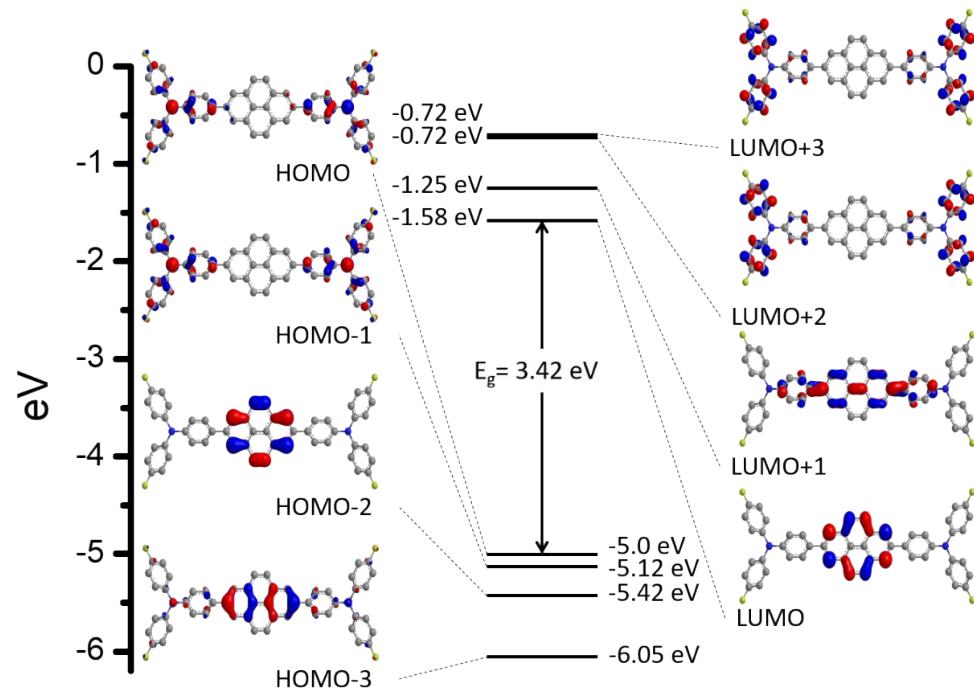
Figure S36. Energy levels and isodensity plots (isodensity contour = 0.04 a.u.) for selected occupied and unoccupied molecular orbitals of **F** obtained by DFT calculations.
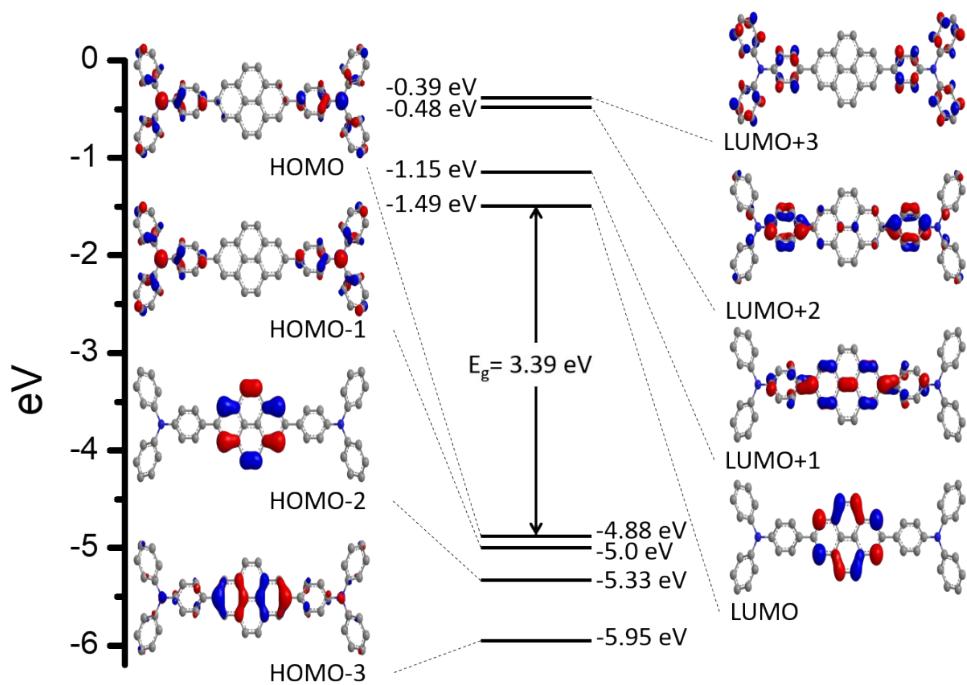
Figure S37. Energy levels and isodensity plots (isodensity contour = 0.04 a.u.) for selected occupied and unoccupied molecular orbitals of **H** obtained by DFT calculations.
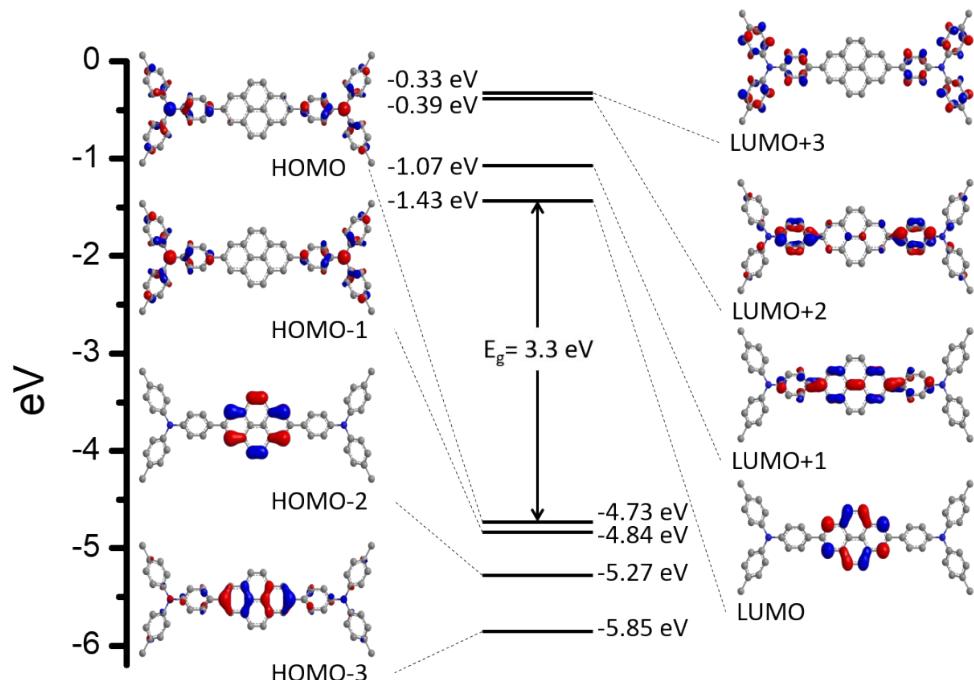
Figure S38. Energy levels and isodensity plots (isodensity contour = 0.04 a.u.) for selected occupied and unoccupied molecular orbitals of **Me** obtained by DFT calculations.
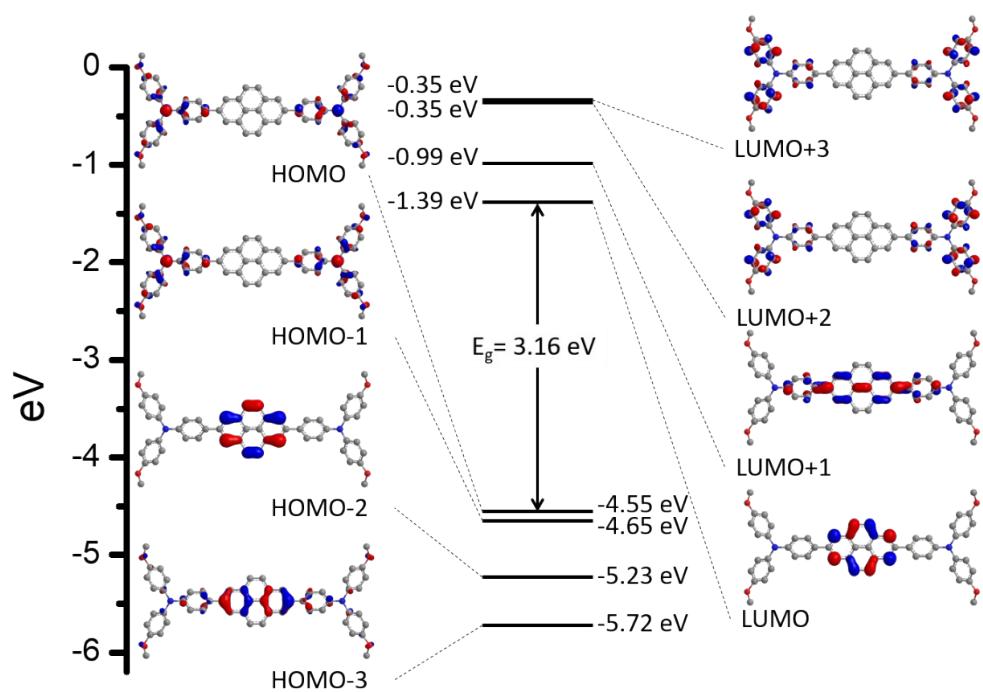
Figure S39. Energy levels and isodensity plots (isodensity contour = 0.04 a.u.) for selected occupied and unoccupied molecular orbitals of **OMe** obtained by DFT calculations.
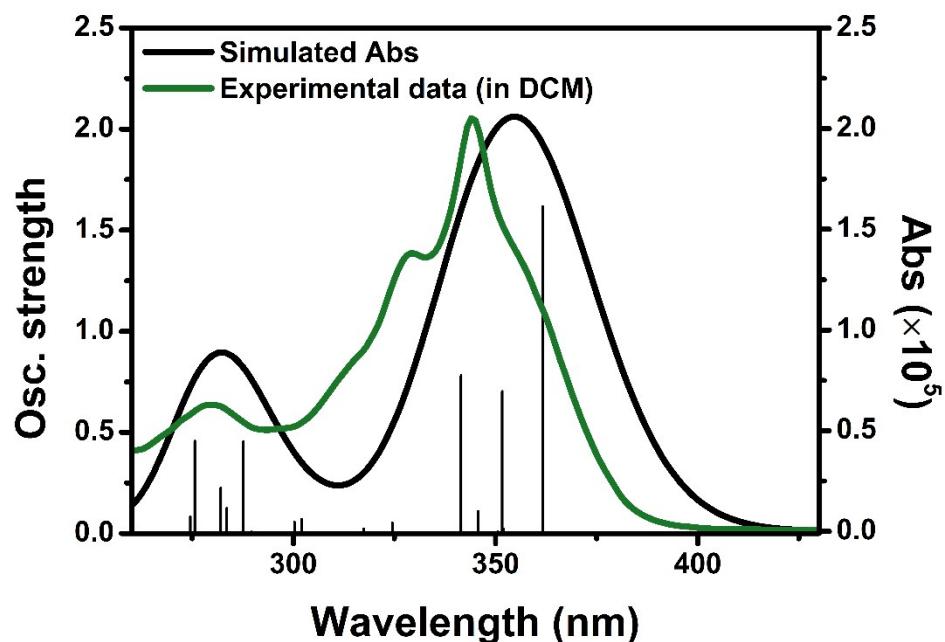
Figure S40. Electronic transition and simulated absorption spectra of **CN** in the ground state geometry obtained by TD-DFT calculations.
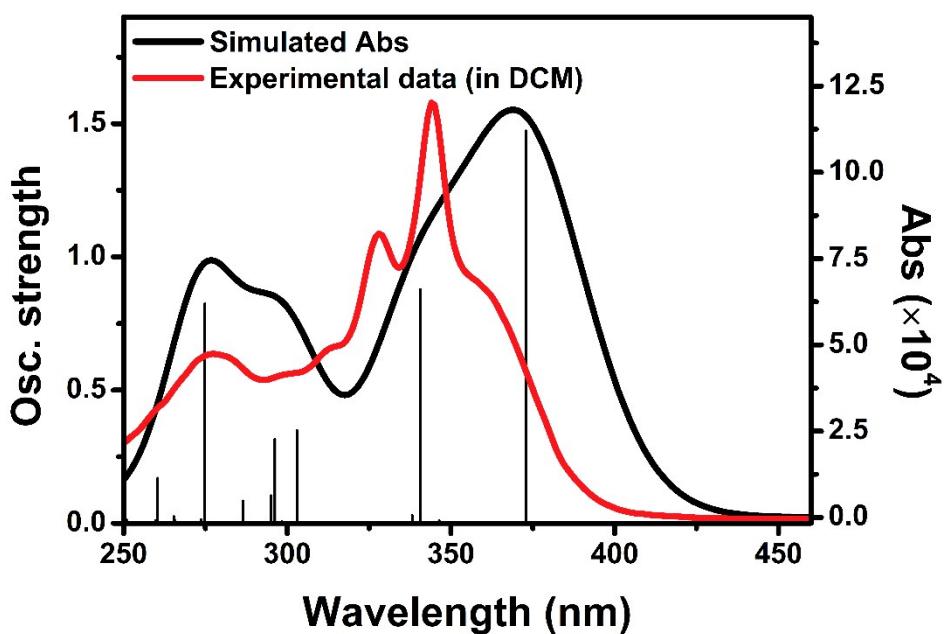
Figure S41. Electronic transition and simulated absorption spectra of **F** in the ground state geometry obtained by TD-DFT calculations.
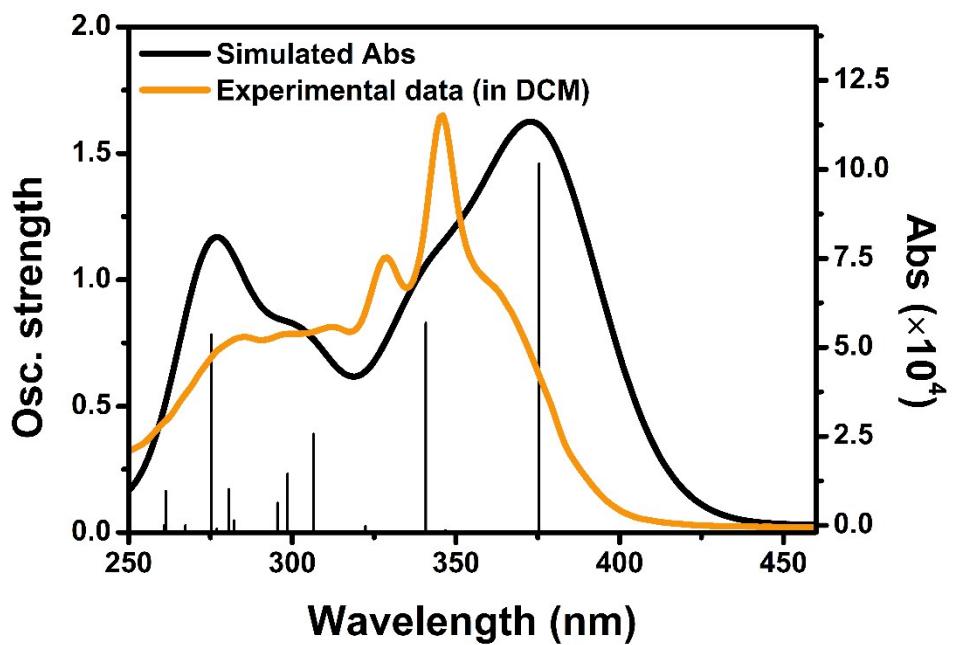
Figure S42. Electronic transition and simulated absorption spectra of **H** in the ground state geometry obtained by TD-DFT calculations.
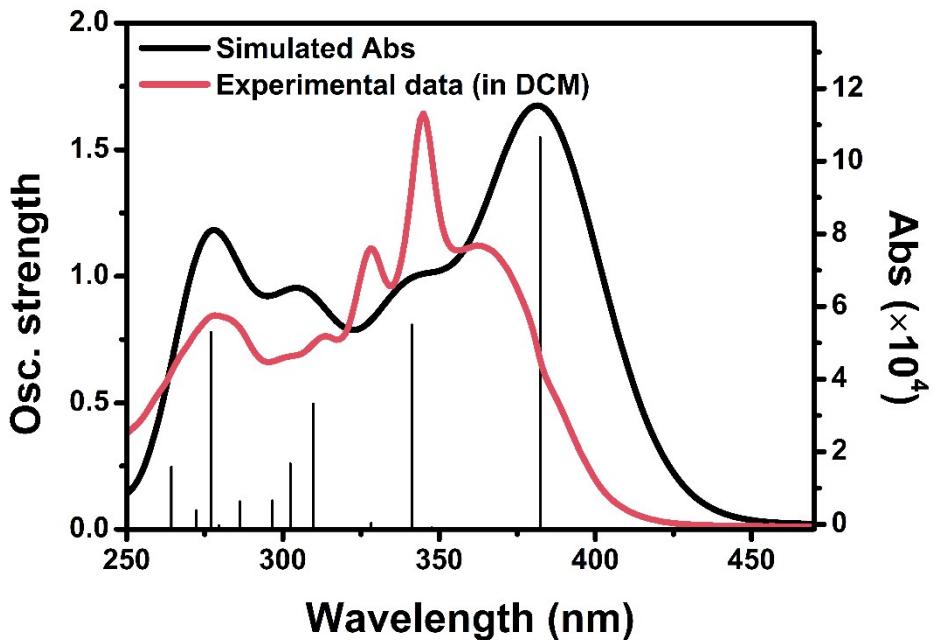
Figure S43. Electronic transition and simulated absorption spectra of **Me** in the ground state geometry obtained by TD-DFT calculations.
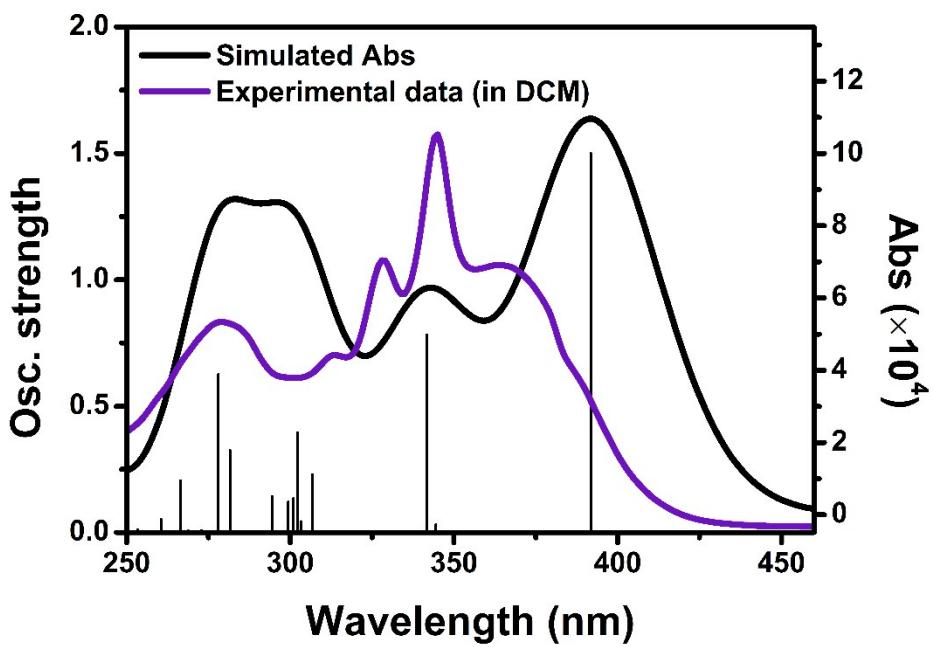

Figure S44. Electronic transition and simulated absorption spectra of **OMe** in the ground state geometry obtained by TD-DFT calculations.

Table S15. TD-DFT calculation: Transition assignment of **CN**

No.	Excitation Energy (cm^{-1})	Wavelength (nm)	Oscillator strength	Assignment
1	26214.00656	381.48	0.0001	H-1->L+1 (35%), HOMO->LUMO (56%)
2	27648.8768	361.68	1.6166	HOMO->L+1 (91%)
3	28403.0104	352.08	0.0214	H-2->LUMO (29%), H-2->L+3 (20%), HOMO->L+2 (50%)
4	28436.88592	351.66	0.7029	H-2->L+2 (28%), HOMO->L+3 (65%)
5	28527.22064	350.54	0.0082	H-2->LUMO (70%), H-2->L+3 (10%), HOMO->L+2 (19%)
6	28931.3072	345.65	0.1107	H-1->L+1 (46%), HOMO->LUMO (40%)
7	29274.0952	341.60	0.0004	H-2->L+1 (87%), HOMO->L+4 (10%)
8	29282.96736	341.50	0.7815	H-1->LUMO (82%)
9	30054.84528	332.73	0	H-1->L+2 (100%)
10	30066.13712	332.60	0.0057	H-1->L+3 (100%)
11	30817.85104	324.49	0.0536	H-2->L+2 (53%), H-2->L+3 (16%), HOMO->L+3 (22%)
12	30819.46416	324.47	0.0186	H-2->L+2 (16%), H-2->L+3 (53%), HOMO->L+2 (22%)
13	31502.62048	317.43	0.0238	H-2->L+6 (38%), HOMO->L+5 (56%)
14	31506.65328	317.39	0.0061	H-2->L+5 (39%), HOMO->L+6 (56%)
15	31927.6776	313.21	0	H-2->L+1 (11%), HOMO->L+4 (85%)
16	32070.43872	311.81	0	H-1->L+4 (96%)
17	33108.48144	302.04	0.0706	H-2->L+4 (80%)
18	33299.63616	300.30	0.0561	H-3->LUMO (67%), H-1->L+1 (16%), H-1->L+7 (14%)
19	34490.11872	289.94	0	H-1->L+5 (96%)
20	34519.15488	289.69	0.0082	H-1->L+6 (95%)

Table S16. TD-DFT calculation: Transition assignment of **F**

No.	Excitation Energy (cm^{-1})	Wavelength (nm)	Oscillator strength	Assignment
1	24317.784	411.22	0.004	HOMO->LUMO (92%)
2	25638.12272	390.04	0	H-1->LUMO (99%)
3	26821.34624	372.84	1.4732	HOMO->L+1 (95%)
4	28499.7976	350.88	0	H-1->L+1 (97%)
5	28867.58896	346.41	0.0111	H-3->LUMO (25%), H-2->L+1 (65%)
6	29357.17088	340.63	0.8783	H-2->LUMO (84%)
7	29568.4896	338.20	0.0296	H-1->L+3 (38%), HOMO->L+2 (59%)
8	29573.32896	338.14	0.0008	H-1->L+2 (39%), HOMO->L+3 (59%)
9	32589.0568	306.85	0	HOMO->L+4 (91%)
10	32993.94992	303.09	0.0001	H-1->L+6 (36%), HOMO->L+5 (60%)
11	33002.01552	303.01	0.3485	H-1->L+5 (35%), HOMO->L+6 (60%)
12	33516.6008	298.36	0.0079	H-1->L+4 (23%), H-1->L+8 (28%), HOMO->L+7 (42%)
13	33612.58144	297.51	0	H-1->L+7 (37%), HOMO->L+8 (57%)
14	33665.00784	297.04	0.0004	H-1->L+2 (58%), HOMO->L+3 (39%)
15	33669.8472	297.00	0.0006	H-1->L+3 (59%), HOMO->L+2 (39%)
16	33756.95568	296.24	0.3164	H-1->L+4 (58%), H-1->L+8 (10%), HOMO->L+7 (16%)
17	33890.03808	295.07	0.1043	H-3->LUMO (67%), H-2->L+1 (26%)
18	34794.9984	287.40	0	H-2->L+4 (73%), H-2->L+9 (14%)
19	34861.13632	286.85	0	H-1->L+11 (33%), HOMO->L+10 (57%)
20	34900.65776	286.53	0.0844	H-1->L+10 (35%), HOMO->L+11 (55%)

Table S17. TD-DFT calculation: Transition assignment of **H**

No.	Excitation Energy (cm^{-1})	Wavelength (nm)	Oscillator strength	Assignment
1	24103.23904	414.88	0.004	HOMO->LUMO (93%)
2	25341.30864	394.61	0	H-1->LUMO (99%)
3	26635.83744	375.43	1.4598	HOMO->L+1 (95%)
4	28251.37712	353.97	0	H-1->L+1 (97%)
5	28834.52	346.81	0.009	H-3->LUMO (27%), H-2->L+1 (65%)
6	29340.23312	340.83	0.8289	H-2->LUMO (84%)
7	31019.49104	322.38	0.0249	H-1->L+4 (39%), HOMO->L+3 (58%)
8	31025.13696	322.32	0.0004	H-1->L+3 (39%), HOMO->L+4 (57%)
9	32451.13504	308.16	0	HOMO->L+2 (93%)
10	32613.2536	306.62	0.0002	H-1->L+6 (37%), HOMO->L+5 (60%)
11	32622.12576	306.54	0.3896	H-1->L+5 (36%), HOMO->L+6 (60%)
12	33498.85648	298.52	0.2319	H-1->L+2 (80%)
13	33844.87072	295.47	0.1172	H-3->LUMO (67%), H-2->L+1 (28%)
14	34869.20192	286.79	0	H-2->L+2 (69%), H-2->L+7 (16%)
15	35236.99328	283.79	0.0005	H-1->L+4 (51%), HOMO->L+3 (34%)
16	35258.7704	283.62	0.0044	H-1->L+3 (57%), HOMO->L+4 (40%)
17	35439.43984	282.17	0.0001	H-1->L+10 (32%), HOMO->L+8 (46%)
18	35441.85952	282.15	0.0473	H-1->L+8 (36%), HOMO->L+10 (53%)
19	35620.10928	280.74	0.1714	H-1->L+11 (37%), HOMO->L+9 (19%), HOMO->L+12 (34%)
20	35654.79136	280.47	0	H-1->L+9 (16%), H-1->L+12 (22%), HOMO->L+11 (54%)

Table S18. TD-DFT calculation: Transition assignment of **Me**

No.	Excitation Energy (cm^{-1})	Wavelength (nm)	Oscillator strength	Assignment
1	23518.48304	425.20	0.004	HOMO->LUMO (95%)
2	24618.63088	406.20	0	H-1->LUMO (99%)
3	26150.28832	382.40	1.5484	HOMO->L+1 (95%)
4	27718.24096	360.77	0	H-1->L+1 (97%)
5	28761.9296	347.68	0.0062	H-3->LUMO (30%), H-2->L+1 (63%)
6	29295.06576	341.35	0.8078	H-2->LUMO (83%)
7	30454.89904	328.35	0.0247	H-1->L+4 (39%), HOMO->L+3 (58%)
8	30459.7384	328.30	0.0022	H-1->L+3 (40%), HOMO->L+4 (57%)
9	32076.08464	311.76	0	HOMO->L+2 (93%)
10	32275.30496	309.83	0.0004	H-1->L+6 (37%), HOMO->L+5 (60%)
11	32286.5968	309.73	0.4963	H-1->L+5 (37%), HOMO->L+6 (59%)
12	33064.12064	302.44	0.2595	H-1->L+2 (80%)
13	33706.94896	296.67	0.1135	H-3->LUMO (65%), H-2->L+1 (31%)
14	34617.5552	288.87	0.0004	H-1->L+4 (56%), HOMO->L+3 (38%)
15	34628.04048	288.78	0.0031	H-1->L+3 (58%), HOMO->L+4 (41%)
16	34911.14304	286.44	0.0001	H-1->L+11 (34%), HOMO->L+8 (52%)
17	34924.048	286.34	0.1101	H-1->L+10 (38%), HOMO->L+9 (52%)
18	34932.92016	286.26	0.0682	H-1->L+8 (37%), HOMO->L+11 (54%)
19	34945.01856	286.16	0	H-1->L+9 (37%), HOMO->L+10 (55%)
20	34982.12032	285.86	0	H-4->LUMO (10%), H-2->L+2 (60%), H-2->L+7 (19%)

Table S19. TD-DFT calculation: Transition assignment of **OMe**

No.	Excitation Energy (cm^{-1})	Wavelength (nm)	Oscillator strength	Assignment
1	22600.61776	442.47	0.0039	HOMO->LUMO (97%)
2	23553.16512	424.57	0	H-1->LUMO (99%)
3	25522.78464	391.81	1.5004	HOMO->L+1 (96%)
4	27010.08128	370.23	0	H-1->L+1 (98%)
5	28664.33584	348.87	0.0038	H-3->LUMO (36%), H-2->L+1 (58%)
6	29035.35344	344.41	0.0312	H-1->L+3 (39%), HOMO->L+2 (58%)
7	29040.1928	344.35	0.0155	H-1->L+2 (40%), HOMO->L+3 (57%)
8	29258.77056	341.78	0.783	H-2->LUMO (82%)
9	31716.35888	315.29	0	HOMO->L+4 (93%)
10	32595.50928	306.79	0.2292	H-1->L+4 (74%)
11	32979.43184	303.22	0.0439	H-1->L+2 (47%), HOMO->L+3 (33%)
12	32982.65808	303.19	0.0057	H-1->L+3 (46%), HOMO->L+2 (32%)
13	33082.67152	302.27	0.002	H-1->L+6 (31%), HOMO->L+5 (48%)
14	33088.31744	302.22	0.3943	H-1->L+5 (30%), HOMO->L+6 (49%)
15	33225.43264	300.97	0.0026	H-1->L+8 (39%), HOMO->L+9 (51%)
16	33230.272	300.93	0.1351	H-1->L+9 (37%), HOMO->L+8 (48%)
17	33407.7152	299.33	0.1211	H-3->LUMO (57%), H-2->L+1 (34%)
18	33903.7496	294.95	0.0001	H-1->L+11 (34%), HOMO->L+10 (54%)
19	33956.176	294.50	0.1427	H-1->L+10 (34%), HOMO->L+11 (50%)
20	34588.51904	289.11	0	HOMO->L+7 (95%)

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