Supporting Information

Crystallization-Induced Planer Chirality by Asymmetric Ferrocene-Appended Tetraazanaphthacene

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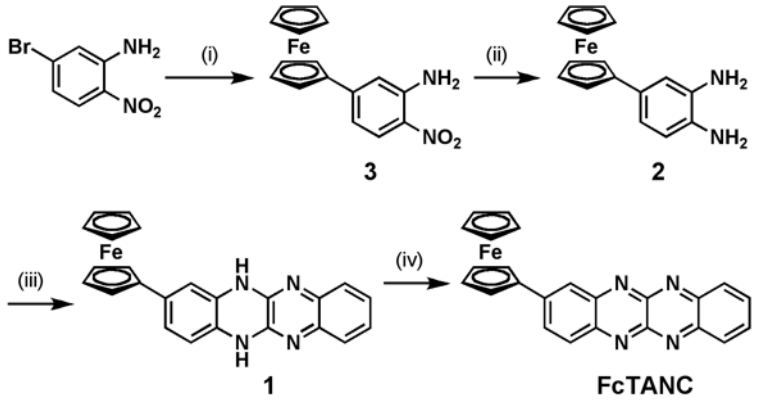
General Methods

^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-LA300 spectrometer. Chemical shift of ^{1}H and ^{13}C NMR signals were quoted to tetramethylsilane (δ = 0.00) and (δ = 77.00) as internal standards, respectively. IR spectra were measured with a HORIBA FREEXACT-II spectrometer. MALDI-TOF mass spectra were collected on a JEOL JMS-S3000 by using dithranol as matrix. Elemental analyses were carried out with Perkin-Elmer instruments Series II CHNS/O Analyzer 2400. Cyclic voltammetry (CV) was carried out in CH_3CN solution of Bu_4NPF_4 (0.10 M) with glassy carbon working, Pt counter, and an Ag/Ag^+ reference electrode using an ALS CHI 600B electrochemical analyzer. All potentials were calibrated with Fc/Fc^+ couple using ferrocene as an internal reference. UV/Vis absorption spectra were measured with a JASCO V-550 UV-*vis* Spectrophotometer spectrometer. The density functional theory (DFT) calculations were carried out using Wavefunction SPARTAN'16 programs. The ground-state geometries were optimized at the B3LYP/6-31G* level of theory.[1] The X-ray data collection for **FcTANC** was performed with a Bruker SMART APEX II CCD X-ray diffractometer using Lorenz-polarization corrections and multilayered confocal mirror MoKα (λ = 0.71070 Å). Data set was processed using APEX2 suite software package (Bruker AXS, Madison USA). These structures of **FcTANC** were solved by direct methods with SHELXS-97[2] or intrinsic phasing with SHELXT 2014/5.[3] The hydrogen-atom positions were geometrically calculated and refined using riding model. All reagents and solvents were purchased from Aldrich, Tokyo Kasei, Kanto Chemical, or Wako, and used as received.



(i) Ferroceneboronic acid, Pd(dppf), NaOHaq, THF,73%, (ii) Pd/C, H_2, EtOH/EtOAc, (iii) DCQ, ethyleneglycol, 83%, (iv) PbO_2, $CHCl_3$, 43%

Scheme S1. The synthesis route of **FcTANC**.

4-Ferrocenyl-2-nitroaniline (3)

The solution of 1-bromo-4-nitro-aniline (1.10 g, 5.00 mmol), ferroceneboronic acid (1.62 g, 7.50 mmol), Pd(dppf)Cl_2 (0.25 g, 0.50 mmol), and NaOHaq (1.0 M, 20 cm^3) in dry THF (20 cm^3) was stirred at 80 °C for 72 h. After cooling to room temperature, the reaction mixture was filtrated with the Celite and THF was evaporated. The reaction mixture was extracted with $CHCl_3$ three times. The combined organic layers were washed with brine, and dried over anhydrous Na_2SO_4. After filtration and evaporation, the crude product was purified by column chromatography (silica, $CHCl_3$), recrystallized with EtOAc / Hexane, and dried under vacuum to afford the product as a black solid (1.2 g, 73%). ^{1}H NMR (300 MHz, $CDCl_3$):δ 8.18 (*s*, 1H, Ar^{1}H), 7.52 (*d*, *J* = 4.35 Hz 1H, Ar^{3}H), 6.77 (*d*, *J* = 4.35 Hz 1H, Ar^{2}H), 6.05 (*s*, 2H, NH_2), 4.59 (*s*, 2H, Fc), 4.31 (*s*, 2H, Fc), 4.05 (*s*, 5H, Fc) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 148.17, 147.85, 177.49, 147.10, 146.53, 144.70, 143.63, 133.25, 132.66, 132.14, 130.38, 130.16, 129.59, 122.10, 82.40, 71.81, 70.34, 67.82 ppm; IR (KBr): 3629, 3594, 3523, 3448, 3323, 2853, 2380, 2175, 1635, 1599, 1560, 1522, 1473, 1414, 1346, 1315, 1290, 1228, 1201, 1173, 1099, 999, 922, 887, 814, 766, 710, 652, 625, 548 cm^{-1}; MS(MALDI-TOF): *m*/*z* = 322.1 $[M]^+$; elemental analysis: calcd (%) for CHNO: C59.65, H 4.38, N17.34; found: C 59.67, H 4.17, N 8.81.

2-Ferrocenyl-5,11-dihydro-5,6,11,12-tetraazanaphthacene (1)

The suspension of **3** (0.97 g, 3.00 mmol), Pd/C (0.10 g) in dried EtOH/EtOAC (40 cm^3 / 40 cm^3) was vigorously stirred under H_2 atmosphere at room temperature overnight. The reaction solution was filtrated with Celite under Ar atmosphere, and evaporated to give 4-ferrocenyl-

1,2-diaminobenzene. Next, the solution of 4-ferrocenyl-1,2-diaminobenzene and 2,3-Dichloroquinoxaline (DCQ) (0.60 g, 3.00 mmol) in ethylene glycol (60 cm^3) was heated for 10 min. After cooling to room temperature, the reaction mixture was poured into water, then filtrated, dried under vacuum to afford the reaction mixture as a yellow solid (1.00 g, 83%). The work up is done without purification because of insolubility in organic solvent. MS(MALDI-TOF): m/z = 418.1 $[M]^+$.

2-Ferrocenyl-5,6,11,12-tetraazanaphthacene (FcTANC)

To a suspension of **2** (0.11 g, 0.26 mmol) and PbO_2 (1.65 g, 6.9 mmol) in $CHCl_3$ (100 cm^3) was vigorously stirred and refluxed for 24 h. After cooling to room temperature, the reaction mixture was filtrated, evaporated, then purified by column chromatography (silica, $CHCl_3$/MeOH = 97:3, v/v), and dried under vacuum to afford the product as a black solid (0.047 g, 43%). ^{1}H NMR (300 MHz, $CDCl_3$):δ 8.39 (*m*, 2H, Ar^8H), 8.31 (*dd*, J = 9.3, 0.6 Hz, 1H, Ar^4H), 8.30 (*dd*, J = 2.1, 0.6 Hz, 1H, Ar^1H), 8.07 (*dd*, J = 9.3, 2.1 Hz, 1H, Ar^3H), 7.95 (*m*, 2H, Ar^7H), 4.97 (*t*, J = 1.8 Hz, 2H, Fc), 4.67 (*t*, J = 1.8 Hz, 2H, Fc), 4.16 (*s*, 5H, Fc) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 142.88, 134.03, 132.38, 128.76, 122.08, 118.89, 83.93, 69.53, 68.96, 65.98 ppm; IR (KBr): 1618, 1541, 1522, 1477, 1454, 1431, 1398, 1377, 1325, 1261, 1107, 1074, 1003, 958, 928, 903, 876, 835, 818, 758, 741, 714, 669, 619, 594, 575, 550, 513 cm^{-1}; elemental analysis: calcd (%) for CHNO: C 69.25, H 3.87, N 13.46; found: C 69.71, H 3.53, N 13.83.

Table S1. Crystal data and structure refinement for **Crystal I** and **Crystal II**.

Identification code (file name)	**Crystal IS** (FerroceneTANC3_100.cif)	**Crystal IR** (FerroceneTANC3_rt_0m_a.cif)	**Crystal II** (FerroceneTANC6_0m_a.cif)
CCDC	1995985	2011490	942335
Empirical formula	$C_{24}H_{16}FeN_4$	$C_{24}H_{16}FeN_4$	$C_{24}H_{16}FeN_4$
Formula weight	416.26	416.26	416.26
Temperature	173(2) K	296(2) K	173(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	*Tetragonal*	*Tetragonal*	*Monoclinic*
Space group	$P4_32_12$	$P4_12_12$	$P2_1/n$
Unit cell dimensions	a = 8.8893(13) Å α = 90°	a = 8.906(3) Å α = 90°	a = 16.111(9) Å α = 90°
	b = 8.8893(13) Å β = 90°	b = 8.906(3) Å β = 90°	b = 10.377(6) Å β = 108.259(8)°
	c = 45.353(7) Å γ = 90°	c = 46.052(16) Å γ = 90°	c = 22.481(13) Å γ = 90°
Volume	3583.8(12) Å^3	3653(3) Å^3	3569(4) Å^3
Z	8	8	8
Density (calculated)	1.543 Mg/m^3	1.514 Mg/m^3	1.549 Mg/m^3
Absorption coefficient	0.860 mm^{-1}	0.844 mm^{-1}	0.864 mm^{-1}
F(000)	1712	1712	1712
Crystal size	0.150 x 0.100 x 0.040 mm^3	0.103 x 0.098 x 0.097 mm^3	0.080 x 0.080 x 0.010 mm^3
Theta range for data collection	2.335 to 27.103°	1.769 to 25.027°	1.865 to 27.484°
Index ranges	-11<=h<=11, -11<=k<=6, -55<=l<=58	-6<=h<=10, -10<=k<=10, -54<=l<=49	-19<=h<=20, -13<=k<=12, -29<=l<=21
Reflections collected	19585	17400	19607
Independent reflections	3964 [R(int) = 0.0762]	3237 [R(int) = 0.0421]	8133 [R(int) = 0.0637]
Completeness to theta = 25.242°	100.0%	100.0 %	99.9%
Data / restraints / parameters	3964 / 0 / 262	3237 / 0 / 262	8133 / 0 / 523
Goodness-of-fit on F^2	0.963	1.049	0.963
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0358, wR_2 = 0.0680	R_1 = 0.0361, wR_2 = 0.0768	R_1 = 0.0517, wR_2 = 0.0973
R indices (all data)	R_1 = 0.0461, wR_2 = 0.0706	R_1 = 0.0465, wR_2 = 0.0819	R_1 = 0.1136, wR_2 = 0.1173
Largest diff. peak and hole	0.406 and -0.310 e.Å^{-3}	0.234 and -0.189 e.Å^{-3}	0.439 and -0.388 e.Å^{-3}

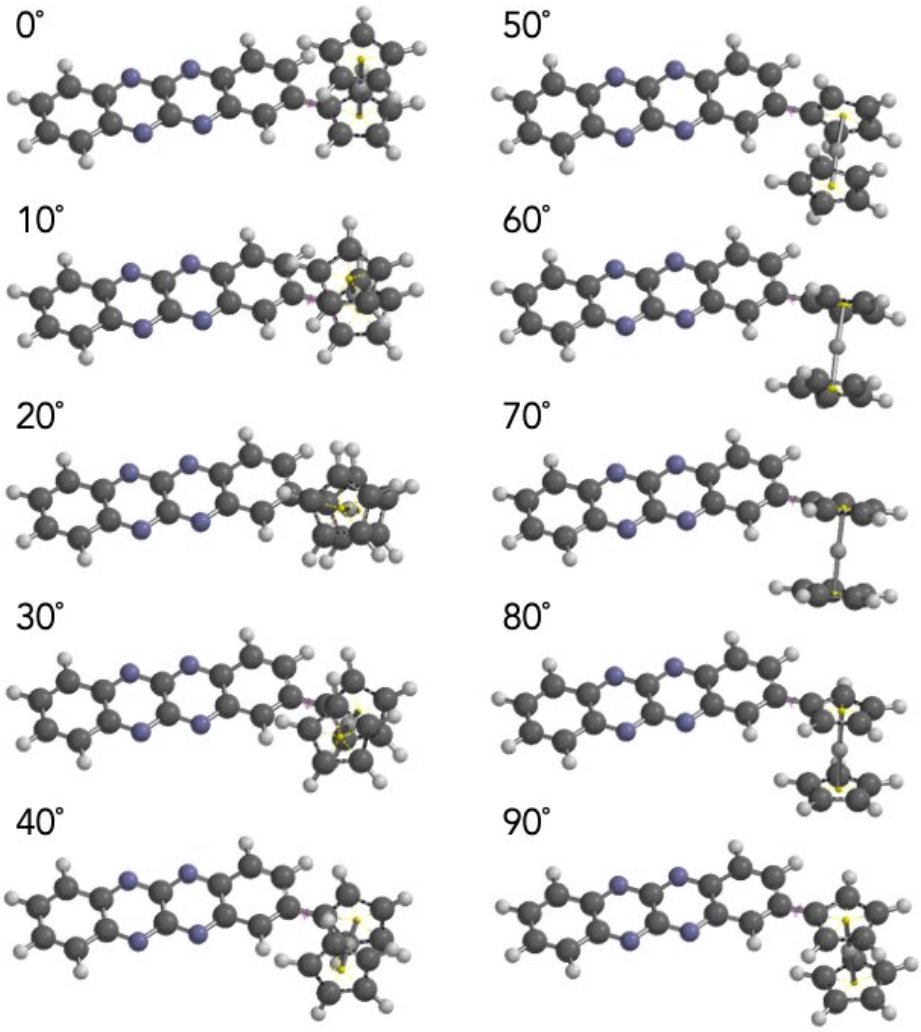


Figure S1. Molecular geometries optimized by DFT calculations at the B3LYP/6-31G** at various torsion angles between Cp of Fc and TANC.

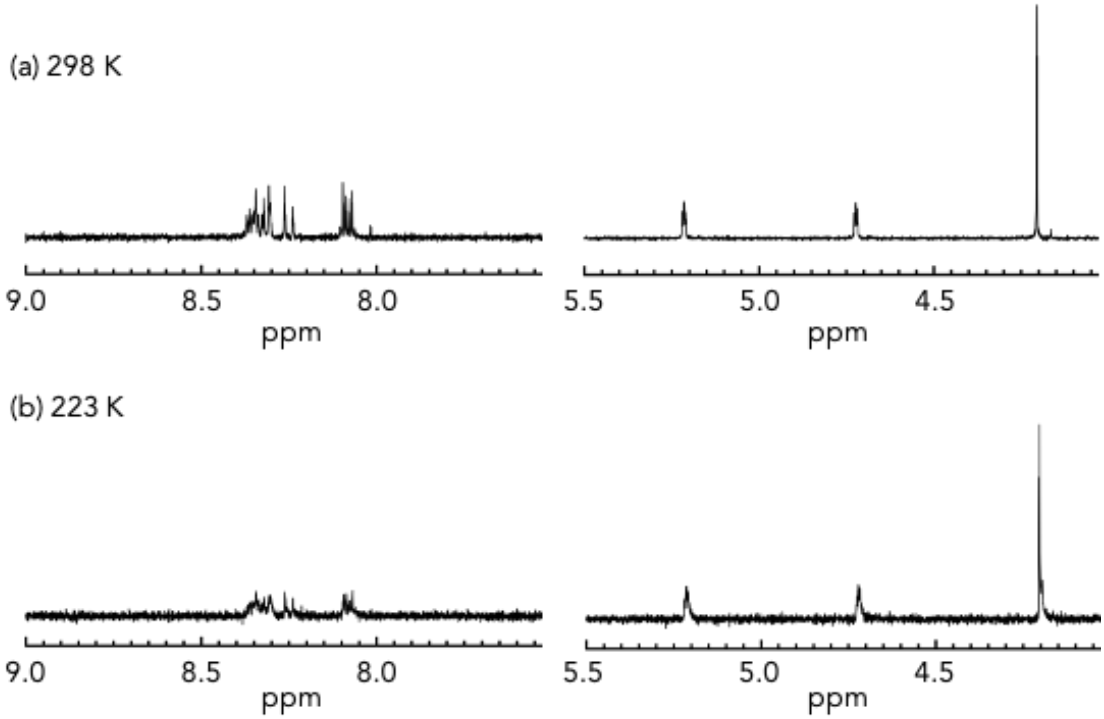


Figure S2. ^{1}H NMR spectra of **FcTANC** in acetone-d_6 solutions at (a) 298 K and (b) 223 K.

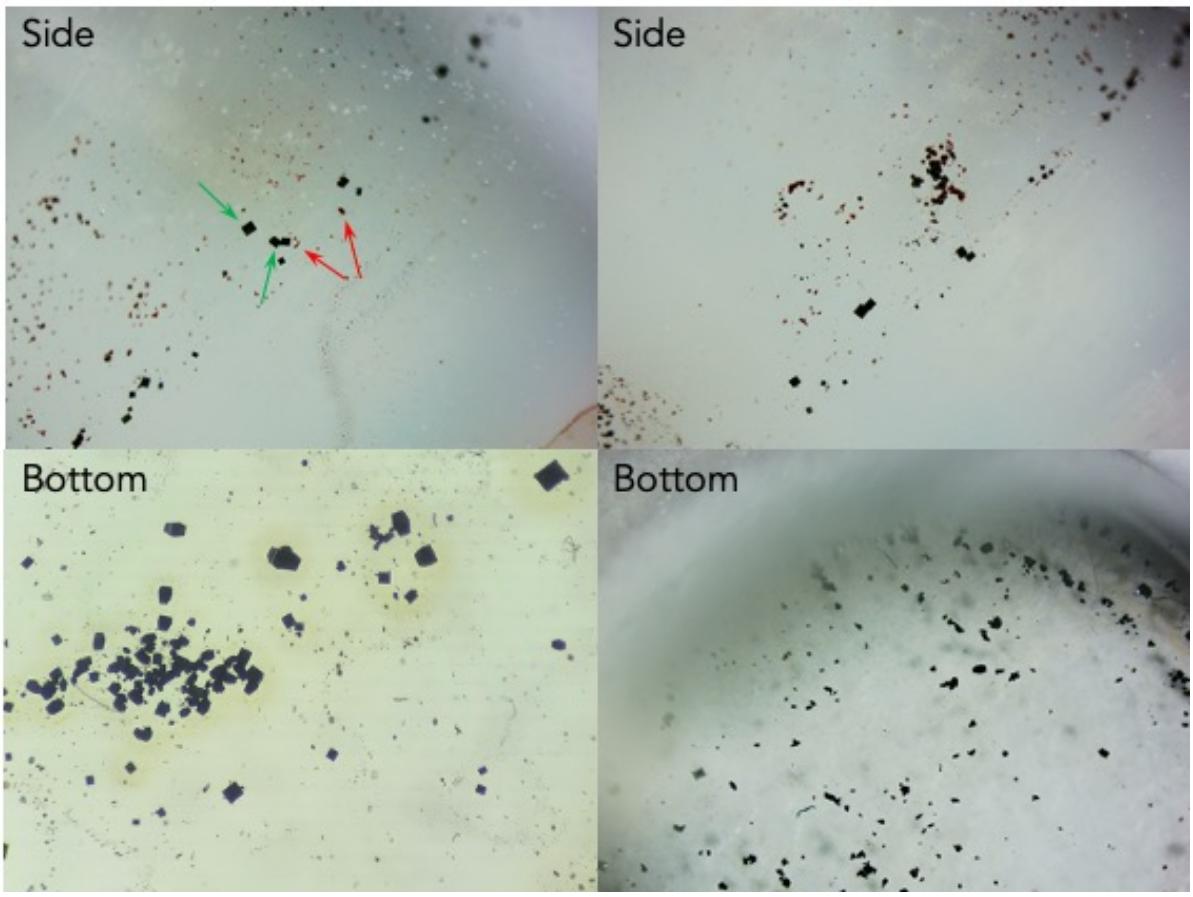


Figure S3. Photographs of Crystal I and Crystal II in glass vials. Red arrows indicate red crystals and green ones indicate green crystals.

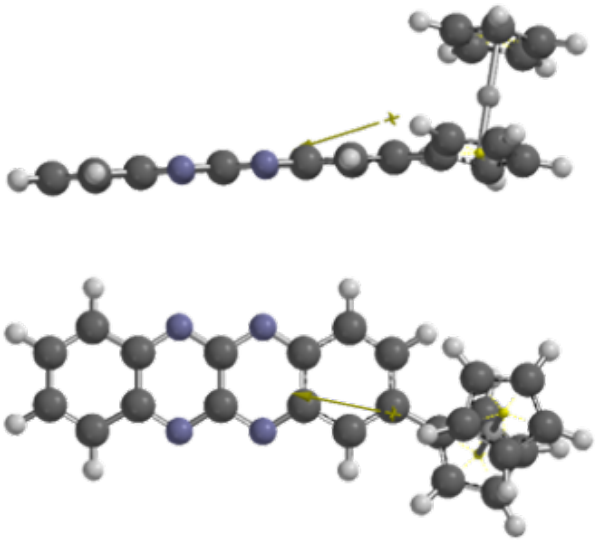


Figure S4. Dipole moment (1.98 debye) of **FcTANC** estimated by DFT calculation at the B3LYP/6-31G**. Arrows indicate the dipole moment.

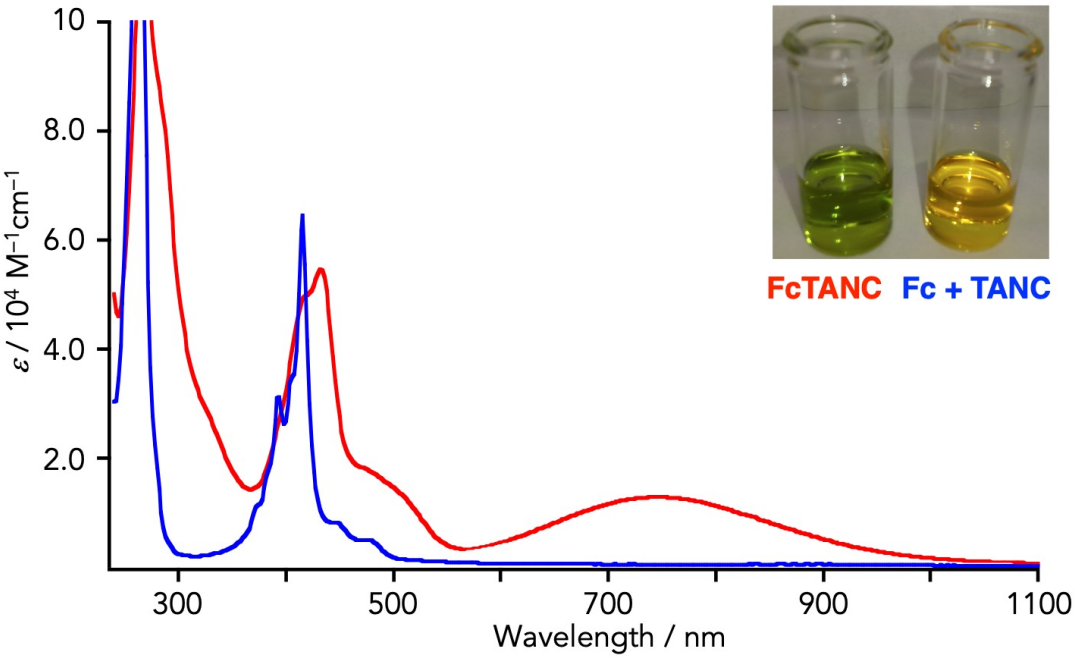


Figure S5. UV-vis absorption spectra of **FcTANC** (red line) and 1:1 mixture (mol) of Fc and TANC (blue line) in $CHCl_3$ (10^{-5} M) and photographs.

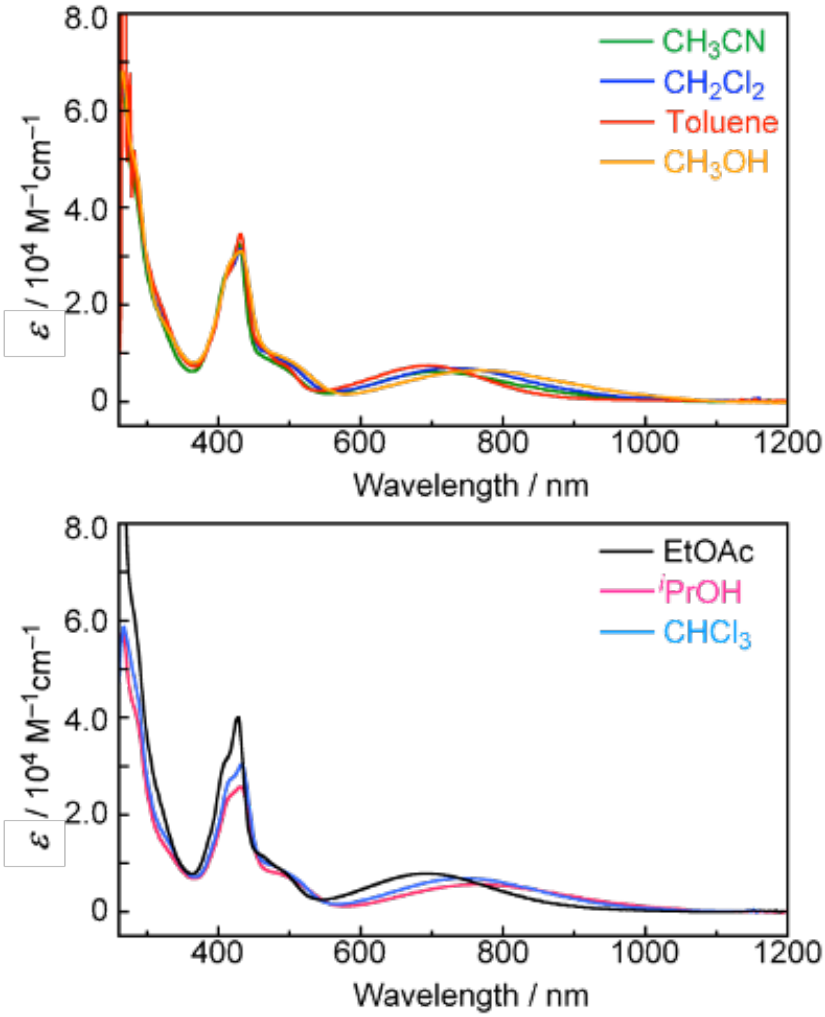


Figure S6. UV–*vis*-NIR spectra of **FcTANC** (10^{-5} M) in various solution states.

Table S2. Relationship between electronic properties of **FcTANC** and parameters of organic solvents.

		MLCT		Kamlet-Taft [a]			Gutmann [b]		Swain [c]		Kosower [d]		
	Protic/aprotic	nm	cm^{-1}	α	β	π^*	*DN*	*AN*	*A*	*B*	*Z*	*Dipole* [e]	ε [f]
Toluene	Aprotic	696	14368	00	11	54	1.0		13	54	-	0.36	2.4
EtOAc	Aprotic	696	14368	00	45	55	17.1	9.3	21	59	64.0	1.88	6.0
CH_3CN	Aprotic	710	14085	19	40	75	14.1	18.9	37	86	71.3	3.92	37
CH_2Cl_2	Aprotic	728	13736	13	10	82	1.0	20.4	33	80	64.7	1.60	9.1
$CHCl_3$	Aprotic	746	13405	20	10	58	40	23.1	42	73	63.2	1.04	4.8
CH_3OH	Protic	766	13055	98	66	60	30.0	41.3	75	50	83.6	1.70	33
$^{i}PrOH$	Protic	770	12987	84	90	52	-	37.3	63	44	78.3	1.66	18

[a] Hydrogen bonding donation α; Hydrogen bonding acceptance β; Polarity/polarizability π^*
[b] Donor Number *DN*; Acceptor Number *AN*
[c] Swain's Acity *A*; Swain's Basity *B*;
[d] Kosower's *Z*

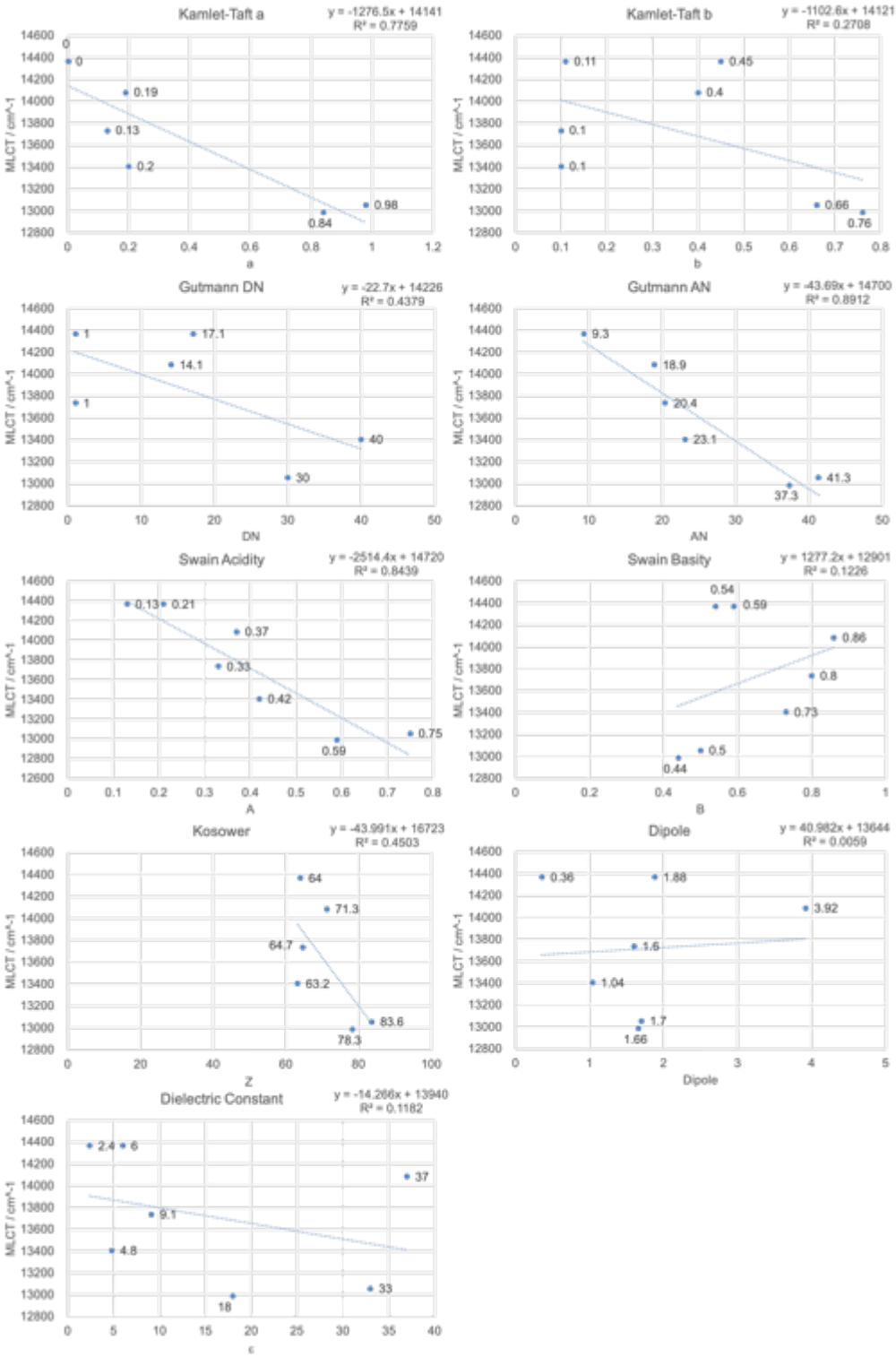


Figure S7. Single-parameter correlations between energy of MLCT band for **FcTANC** and different solvent parameters.

Table S3. Comparison of HOMO, LUMO, and E_{gap} for **FcTANC**, TANC and Fc.

	HOMO / eV	LUMO / eV	E_{gap} / eV
FcTANC[a]	-4.95	-3.97	-0.98
TANC[b]	-	-4.00	2.90[c]
Fc	-4.80	-	-

[a] Calculated by CV measurements.

[b] Referred from 5

[c] Estimated from the onset position of the UV–vis absorption spectrum in CH_2Cl_2: $E_g^{opt} = 1240/\lambda_{onset}$.

References

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