Electronic Supplementary Information (ESI) for

Symmetrically Substituted Siloles on Their 2,5-Positions with Electron-Accepting and Donating Moieties: Facile Synthesis, Aggregation-Enhanced Emission, Solvatochromism, and Device Application

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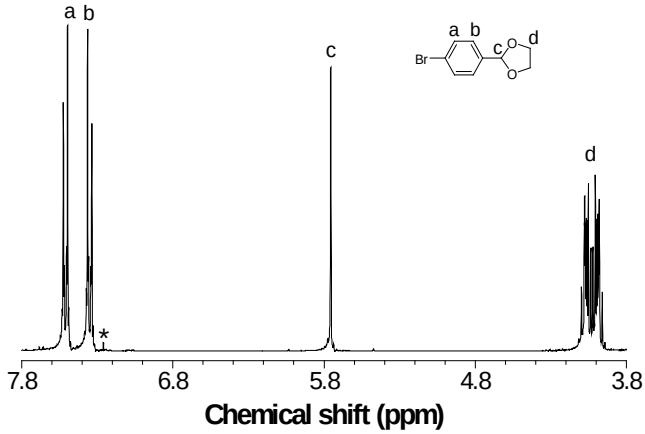

Figure S1. ^{1}H NMR spectrum of **4** in $CDCl_3$. The solvent peak is marked with asterisk.

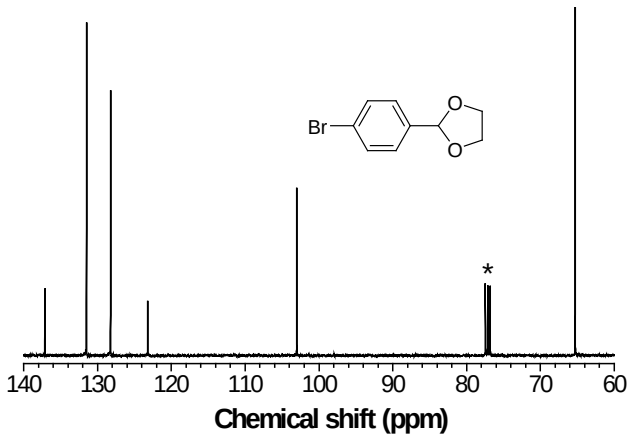

Figure S2. ^{13}C NMR spectrum of **4** in $CDCl_3$. The solvent peak is marked with asterisk.

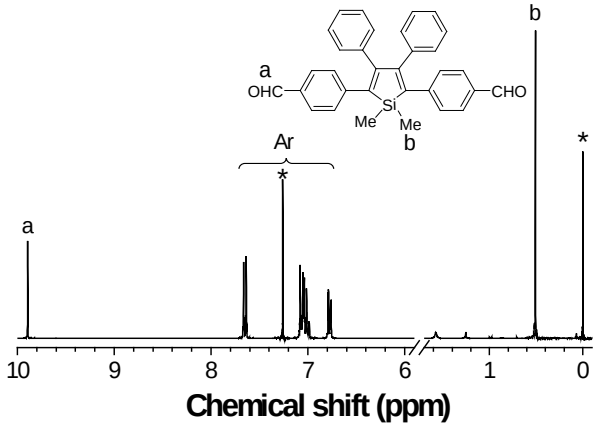

Figure S3. ^{1}H NMR spectrum of DMTPS-ALD in $CDCl_3$.The solvent peaks are marked with asterisks.

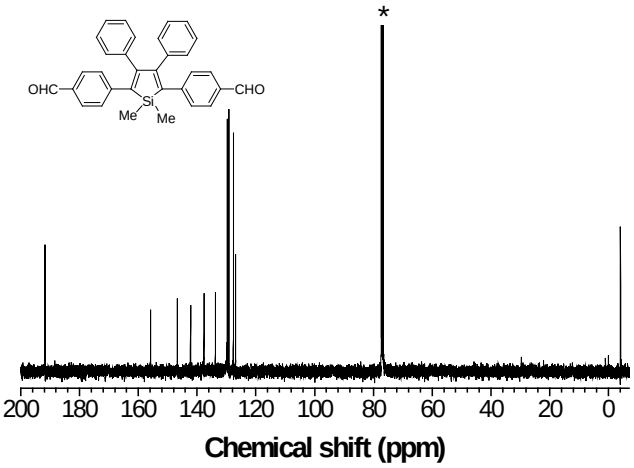

Figure S4. ^{13}C NMR spectrum of DMTPS-ALD in $CDCl_3$. The solvent peak is marked with asterisk.

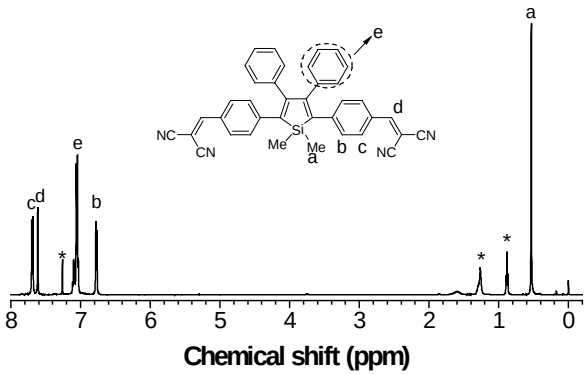

Figure S5. ^{1}H NMR spectrum of DMTPS-DCV in $CDCl_3$. The solvent peaks are marked with asterisks.

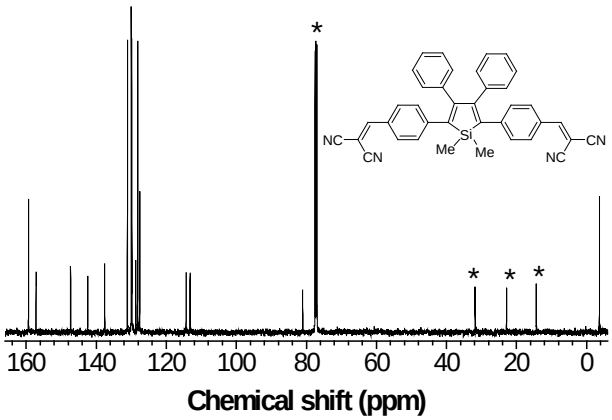

Figure S6. ^{13}C NMR spectrum of DMTPS-DCV in $CDCl_3$. The solvent peaks are marked with asterisks.

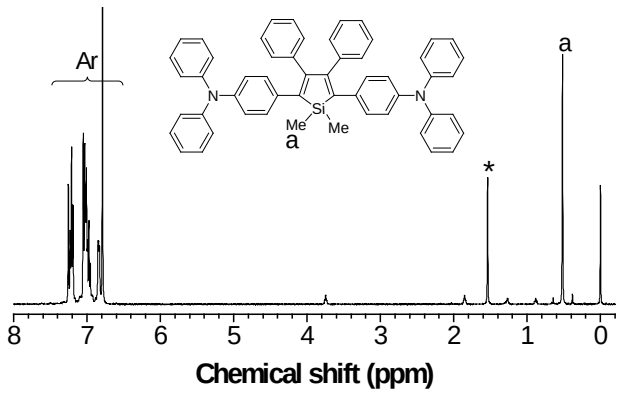

Figure S7. ^{1}H NMR spectrum of DMTPS-DPA in $CDCl_3$. The solvent peaks are marked with asterisks.

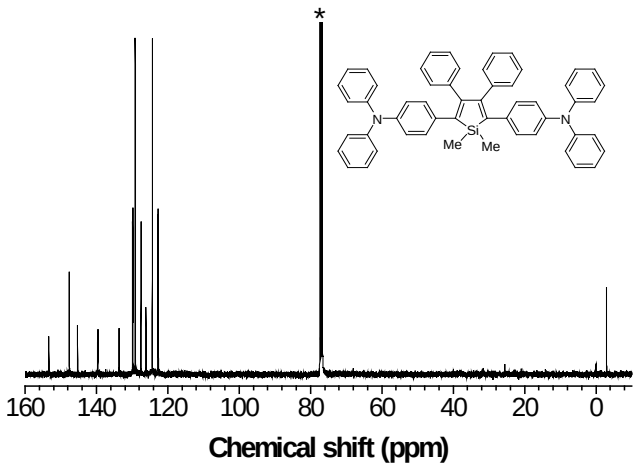

Figure S8. ^{13}C NMR spectrum of DMTPS-DPA in $CDCl_3$. The solvent peak is marked with asterisk.

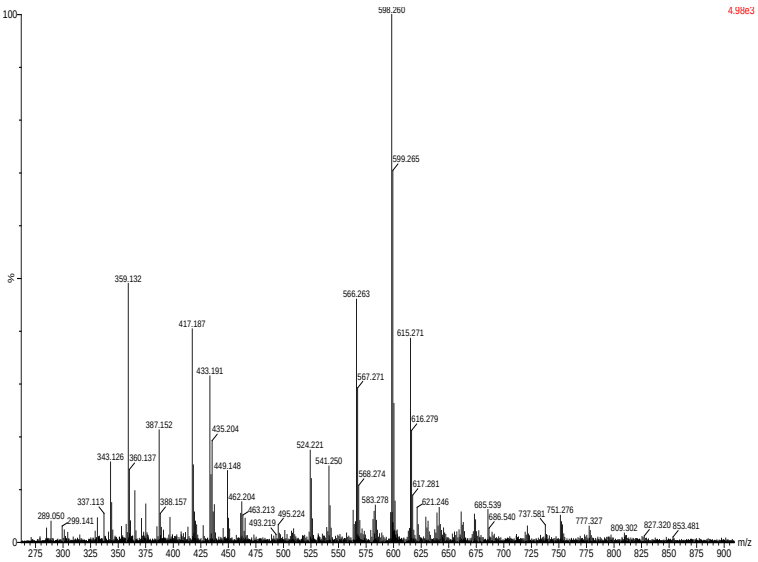

Figure S9. High resolution mass (HRMS) spectrum of DMTPS-DCV.

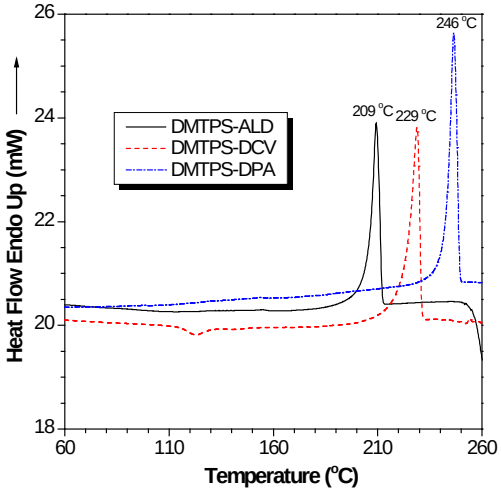

Figure S10. DSC graphs of silole derivatives. Heating rate: 10 °C/min, atmosphere: N_2.

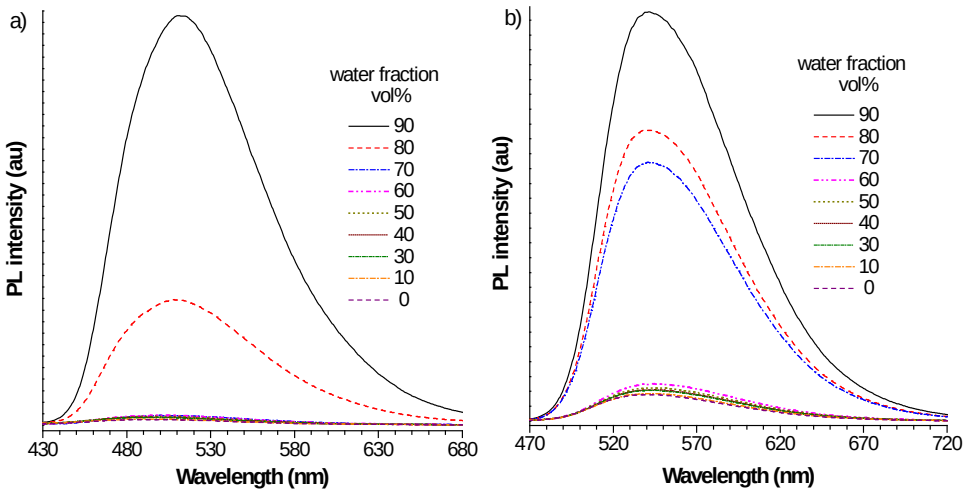

Figure S11. PL spectra of DMTPS-ALD (a) and DMTPS-DPA (b) in THF/water mixtures with different water fraction at room temperature. λ_{ex} = 377 and 422 nm, concentration = 20 and 10 μM, respectively.

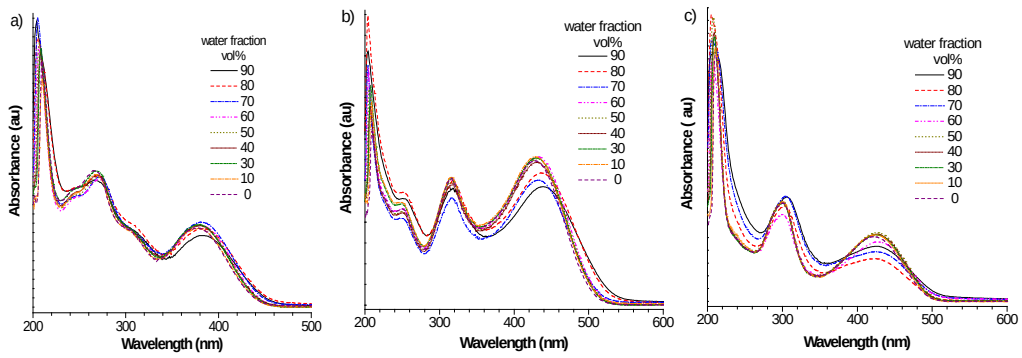

Figure S12. Absorption spectra of (a) DMTPS-ALD, concentration (*c*) = 20 μM, (b) DMTPS-DCV, *c* = 10 μM, and (c) DMTPS-DPA, *c* = 10 μM in THF/water mixtures with different water fraction at room temperature.

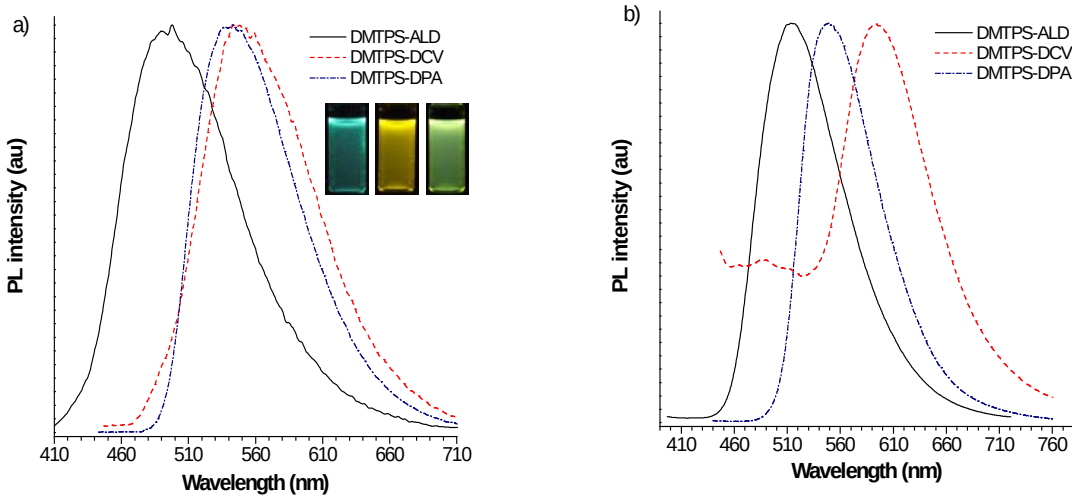

Figure S13. PL spectra of silole derivatives in (a) THF solution (concentration: 2×10^{-4} M) and (b) film states, respectively. The inset in panel (a) is the corresponding photographs of their solutions taken under UV lamp (365 nm).

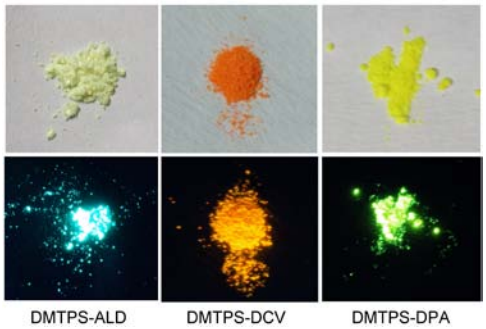

Figure S14. Photographs of silole derivatives under ambient light (top panel) and UV light (bottom panel).

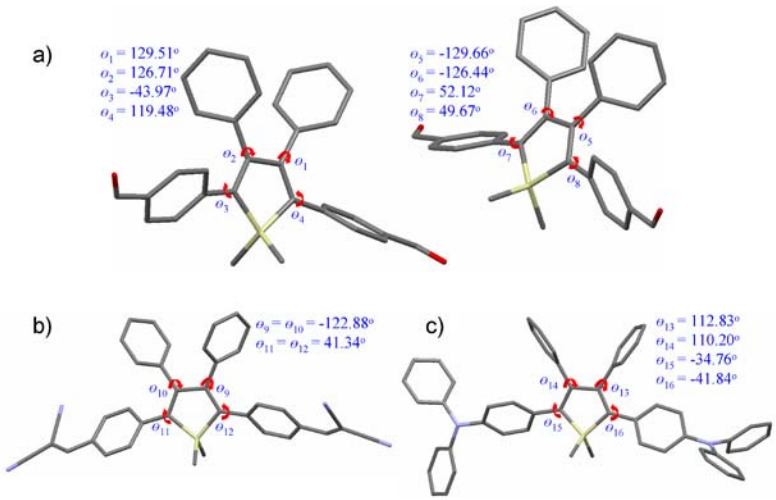

Figure S15. Molecular structures and torsion angles of (a) DMTPS-ALD, (b) DMTPS-DCV and (c) DMTPS-DPA. The atoms are represented as sticks in all panels. Si, N, O, and C atoms are in light yellow, purple, red, and grey, respectively. All the H atoms are omitted for clarity.

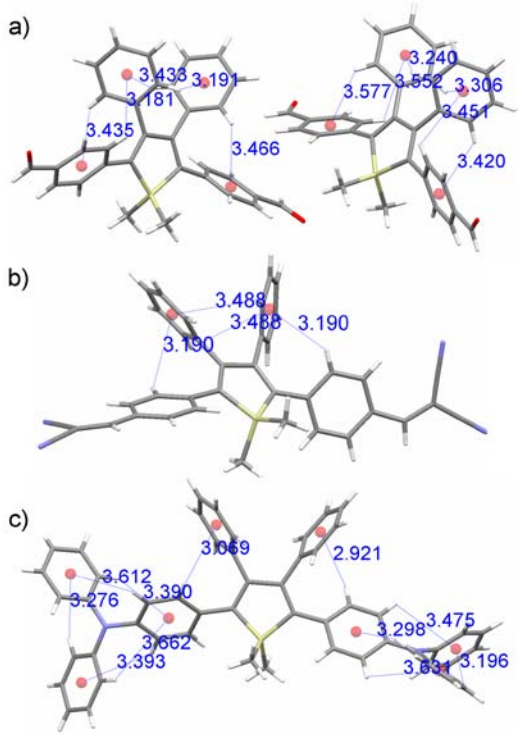

Figure S16. Representative intramolecular C-H···π interactions with indicated distances (Å) of (a) DMTPS-ALD, (b) DMTPS-DCV and (c) DMTPS-DPA.

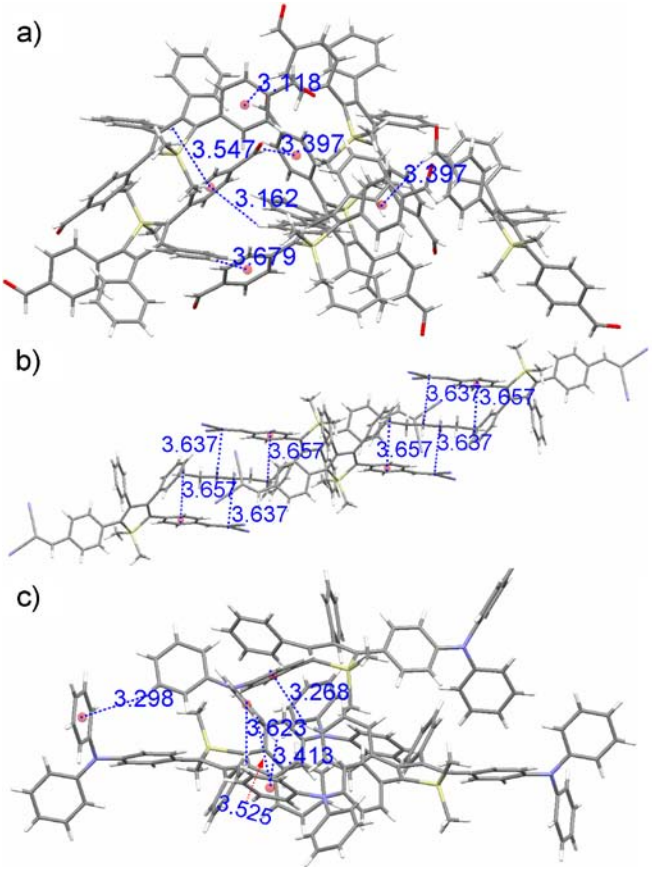

Figure S17. Representative intermolecular C-H…π interactions with indicative distances (Å) of (a) DMTPS-ALD, (b) DMTPS-DCV and (c) DMTPS-DPA. Panel (b) also shows the J-aggregation interaction of DMTPS-DCV.

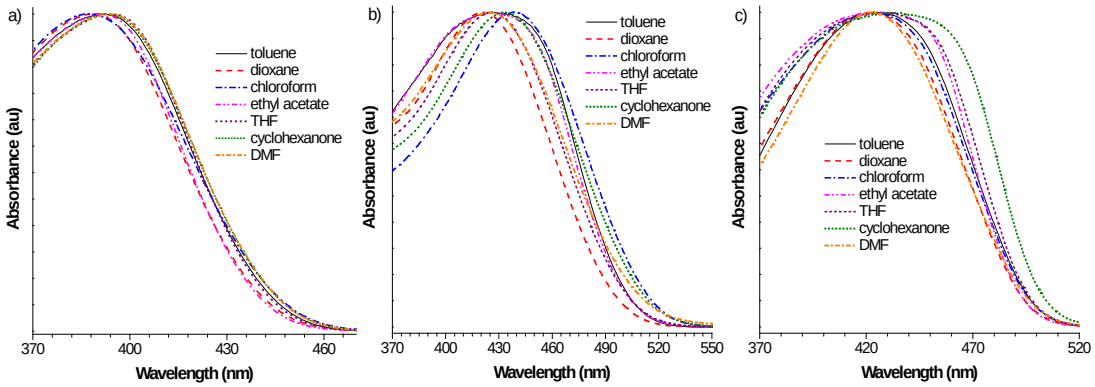

Figure S18. Normalized absorption spectra of DMTPS-ALD (a), DMTPS-DCV (b), and DMTPS-DPA (c) in solvents with varying polarity. Concentration: 2×10^{-4} M.

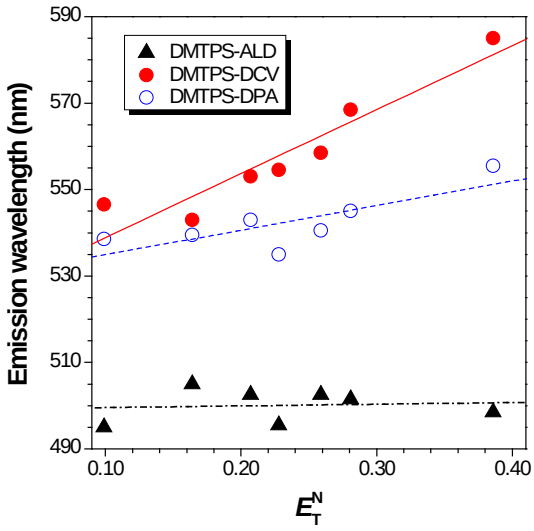

Figure S19. The dependency of the emission wavelengths of silole derivatives on the empirical parameters (E_T^N) of solvent polarity. Where,

$$E_T^N = \frac{E_T(\text{solvent}) - E_T(\text{TMS})}{E_T(\text{water}) - E_T(\text{TMS})} = \frac{E_T(\text{solvent}) - 30.7}{32.4} \quad \text{(TMS = tetramethylsilane)}$$

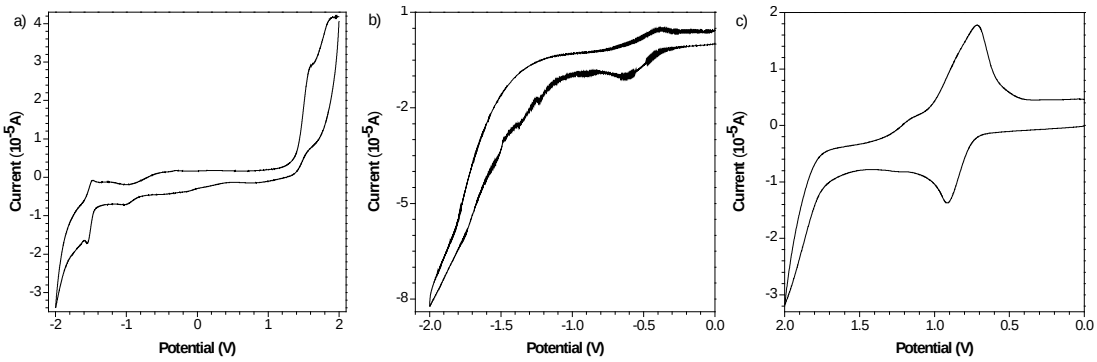

Figure S20. The cyclic voltammograms of DMTPS-ALD (a), DMTPS-DCV (b), and TMTPS-DPA (c) in CH_2Cl_2/ 0.1M $[^nBu_4N]^+[PF_6]^-$at a rate of 50 mV s^{-1}.

Table S1. Crystal Data and Structure Refinement for DMTPS-ALD

Empirical formula	$C_{32}H_{26}O_2Si$
Formula weight	470.62
Temperature	173(2) K
Wavelength	1.54178 Å
Crystal system	Orthorhombic
Space group	Pbca
Unit cell dimensions	a = 21.7477(9) Å □α = 90°
	b = 13.4689(6) Å β = 90°
	c = 35.5044(11) Å γ = 90°
Volume	10399.9(7) $Å^3$
Z	16
Density (calculated)	1.202 mg m^{-3}
Absorption coefficient	0.996 mm^{-1}
F(000)	3968
Crystal size	0.30 × 0.07 × 0.06 mm^3
Theta range for data collection	2.49 to 67.49°.
Index ranges	$-25 \leq h \leq 23$,
	$-14 \leq k \leq 16$
	$-42 \leq l \leq 31$
Reflections collected	28501
Independent reflections	9219 [R(int) = 0.0610]
Completeness to theta = 66.50°	98.4 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00 and 0.81
Refinement method	Full-matrix least-squares on F2
Data / restraints / parameters	9219 / 0 / 635
Goodness-of-fit on F2	1.015
Final R indices [I>2sigma(I)]	R1 = 0.0456, wR2 = 0.0770
R indices (all data)	R1 = 0.0958, wR2 = 0.0847
Largest diff. peak and hole	0.485 and -0.283 e.$Å^{-3}$

Table S2. Crystal Data and Structure Refinement for DMTPS-DPA.

Empirical formula	$C_{54}H_{44}N_2Si$
Formula weight	749.00
Temperature	133(2) K
Wavelength	1.5418 Å
Crystal system	Monoclinic
Space group	P2(1)/c
Unit cell dimensions	a = 20.3587(4) Å α = 90°
	b = 11.0369(3) Å β = 93.111(2)°
	c = 18.2729(8) Å γ = 90°
Volume	4099.8(2) $Å^3$
Z	4
Density (calculated)	1.213 mg m^{-3}
Absorption coefficient	0.800 mm^{-1}
F(000)	1584
Crystal size	0.40 × 0.37 × 0.07 mm^3
Theta range for data collection	4.35 to 67.47°.
Index ranges	$-15 \leq h \leq 24$
	$-13 \leq k \leq 10$
	$-21 \leq l \leq 21$
Reflections collected	13752
Independent reflections	7105 [R(int) = 0.0273]
Completeness to theta = 66.50°	96.3 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00 and 0.66
Refinement method	Full-matrix least-squares on F2
Data / restraints / parameters	7105 / 0 / 516
Goodness-of-fit on F^2	1.020
Final R indices [I>2sigma(I)]	R1 = 0.0371, wR2 = 0.0902
R indices (all data)	R1 = 0.0485, wR2 = 0.0933
Largest diff. peak and hole	0.288 and -0.283 e.$Å^{-3}$