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Tetrakis(trialkylsilylethynylphenyl)ethenes: Mechanofluorochromism Arising From Steric Considerations With Unusual Crystal Structure

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I. Synthetic scheme



Scheme S1. Structural motifs containing phenyl substituted olefinic and extended olefinic backbone with wide scope for MFC

II. Experimental section

Materials and methods

TLC analyses were performed using Merck TLC silica gel 60 F254 and silica gel (RANKEM, spherical, 75–150 mm) was used for column chromatography. Palladium(II) chloride was purchased from RANKEM. CuI was obtained from FINAR & Co., Inc. The solvents, DIPA, THF and DCM were purchased from RANKEM & Co., Inc and used as received. The deuterated solvents were purchased from MERCK & Co., Inc. The compounds benzophenone and tetraiodo benzophenone were synthesized following literature procedures. The target molecules were prepared using a procedure similar to reported.

Instrumentation

¹H, ¹³C, DEPT, HMBC and HSQC NMR spectra were recorded on a BRUKER AVANCE 400 and BRUKER AVANCE 500 spectrometer (400 or 500 MHz for ¹H and 100 or 125 MHz for ¹³C NMR). The chemical shift values of ¹H NMR are expressed in parts per million downfield relative to the internal standard, tetramethylsilane ($\delta = 0$ ppm) or chloroform ($\delta = 7.26$ ppm). Splitting patterns are indicated as s, singlet; d, doublet; t, triplet, q, quartet; m, multiplet. UV-Visible absorption spectra were recorded on a JASCO V-630 spectrophotometer. Fluorescence spectra were measured on Jasco FP-6300 or Horiba JOBIN YVON FLUOROLOG-3-11 spectrofluorimeter. Time-resolved fluorescence measurements were performed on Horiba Jobin Yvon TCSPC lifetime instrument in a time-correlated, single-photon counting arrangement. 360 nm nano-LED was used as a light source. The absolute photoluminescence quantum yield (PLQY) was collected by measuring the total light output in all directions in an integrating sphere using EDINBURGH (UK) and FLS 980 TCSPC instruments. The fluorescence images of the crystals of the luminophores were taken using MOTIC microscope with the help of a hand-held UV lamp. Infrared spectra (IR) were recorded on a PERKIN ELMER Spectrum1 FTIR instrument. Raman analysis was performed on BRUKER RFS 27: Stand alone FT-Raman spectrometer. Single crystal X-ray diffraction study was done on a BRUKER AXS KAPPA APEX2 CCD diffractometer. Powder XRD was recorded using a BRUKER D8 ADVANCE diffractometer equipped with a Cu anode and Cu Ka of the wavelength of 1.5406 Å. Thermo gravimetrical analysis was performed using TA INSTRUMENTS O-500 Hi-Res-TGA and differential scanning calorimetric measurements were done using TA INSTRUMENTS Q-200 MDSC. Elemental analysis was carried out using ELEMENTAR MAKE, VARIO MICRO CUBE analyzer. The ground state geometries were determined using density functional theory (DFT) and time dependent density functional theory (TD-DFT) with Becke's three-parameter functional and the Lee-Yang–Parr functional (B3LYP)^[4] using the 6-31G* basis set^[5]. All calculations were performed using the Gaussian 09 program package^[6]. TD-DFT results were extracted using GaussSum 3.0^[7].

III. Synthesis of the intermediates and target molecules^[1,2]



General procedure^[3] for the synthesis of TPE(TIPS)₄ and TPE(TMS)₄

To a degassed solution of tetraiodo tetraphenylethylene (1 eq.), $PdCl_2(PPh_3)_2$ (8 mol %), CuI (8 mol %) in a 1:1 mixture of solvents, THF/DIPA, was added TIPS or TMS-actylene (5 eq.) and the resulting mixture was stirred at 80 °C for 24 h. The solvents were removed under high vacuum and the crude product was dissolved in DCM and extracted with water three times and finally washed with brine solution. The organic layer was separated and dried over anhydrous Na₂SO₄. The solvent was removed under vacuum and the crude product was purified through column chromatography using hexane as eluent.

TPE(TIPS)₄ **[1,1,2,2-tetrakis(4-((triisopropylsilyl)ethynyl)phenyl)ethene]**: Off-white solid. Yield: 91.6 %. ¹H NMR (400 MHz, CDCl₃): δ (ppm) = 7.23 (d, *J*= 8.4 Hz, 4H), 6.92 (d, *J*= 8.4 Hz, 4H), 1.12 (s, 84H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) =143.29, 140.8, 131.8, 131.3, 122.0, 107.2, 91.4, 18.8, 11.5. IR (KBr): ν , cm⁻¹ = 3032, 2951, 2862, 2349, 2155, 1914, 1500, 1461, 1403, 1247, 1224, 1180, 1106, 1069, 1015, 994, 917, 871, 834, 758, 638, 571, 538. HRMS (ESI) m/z: (M+H)⁺ calcd for C₇₀H₁₀₀Si₄, 1053.6980; found, 1053.6984. Anal calcd for C₇₀H₁₀₀Si₄: C, 79.78; H, 9.56; Si, 10.66. Found: C, 79.75; 9.36.

TPE(TMS)₄ **[1,1,2,2-tetrakis(4-((trimethylsilyl)ethynyl)phenyl)ethene]**: Off-white solid. Yield: 94 %. ¹H NMR (400 MHz, CDCl₃): δ (ppm) = 7.20 (d, *J*= 8.4 Hz, 4H), 6.88 (d, *J*= 8.4 Hz, 4H), 0.229 (s, 36H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) = 143.2, 140.9, 131.7, 131.3, 121.7, 105.0, 95.0, 0.07. IR (KBr): *v*, cm⁻¹ = 2955, 2345, 2153, 1800, 1499, 1403, 1247, 1222, 1104, 1016, 867, 837, 787, 760, 701, 639, 602, 569, 538. HRMS (ESI) (m/z): (M+H)⁺ calcd for C₄₆H₅₂Si₄, 717.3224; found, 717.3212. Anal calcd for C₄₆H₅₂Si₄: C, 77.03; 7.31; Si, 10.66. Found: C, 76.95; H, 7.25.

IV. Solution NMR analysis



Figure S2. Expansion of ¹H NMR spectrum of TPE(TIPS)₄

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Figure S4. Expansion of ¹³C NMR spectrum of TPE(TIPS)₄



Figure S6. Expansion of DEPT NMR spectrum of TPE(TIPS)₄



Figure S7. ¹H-¹H COSY NMR spectrum of TPE(TIPS)₄



Figure S8. Expansion of ¹H-¹H COSY NMR spectrum of TPE(TIPS)₄







Figure S10. HSQC NMR spectrum (expansion) of TPE(TIPS)₄



Figure S11. HMBC NMR spectrum (expansion) of TPE(TIPS)₄



Figure S12. HMBC NMR spectrum (expansion) of TPE(TIPS)₄



Figure S14. Expansion of ¹H NMR spectrum of TPE(TMS)₄



Figure S16. Expansion of ¹³C NMR spectrum of TPE(TMS)₄





Figure S18. Expansion of ¹H-¹H COSY NMR spectrum of TPE(TMS)₄



Figure S20. Expansion of DEPT NMR spectrum of TPE(TMS)₄



Figure S21. HSQC NMR spectrum of TPE(TMS)₄



Figure S22. Expansion of HSQC NMR spectrum of TPE(TMS)₄



Figure S23. HMBC NMR spectrum of TPE(TMS)₄



Figure S24. Expansion of HMBC NMR spectrum of TPE(TMS)₄

V. ESI-MASS Analysis



Figure S25. ESI-MASS spectrum of TPE(TMS)₄

Elemental Composition Report

Single Mass Analysis Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0 Element prediction: Off Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Odd and Even Electron Ions 4 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass) Elements Used: C: 0-70 H: 0-101 Si: 0-4



Figure S26. ESI-MASS spectrum of TPE(TIPS)₄

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VI. Data of X-ray crystallographic analysis of compound TPE(TMS)₄:

CCDC–1555003 contains the supplementary crystallographic data for **1**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via <u>www.ccdc.cam.ac.uk/data_request/cif</u>.

C46H52Si4
717.24
296(2) K
0.71073 A
Orthorhombic
Iba2
$a = 15.856(4) \text{ Å} \qquad \alpha = 90^{\circ}$
$b = 28.435(7) \text{ Å} \qquad \beta = 90^{\circ}$
$c = 10.3986(19) \text{ Å} \qquad \gamma = 90^{\circ}$
4688.3(18) Å ³
4
1.016 g/cm ³
0.154 mm ⁻¹
1536.0
0.250 x 0.220 x 0.130 mm ³
$MoK_{\alpha}(\lambda = 0.71073)$
5.008 to 49.99°
-18<=h<=18, -33<=k<=26, -12<=l<=12
15687
$4109 [R(int) = 0.0703, R_{sigma} = 0.0806]$
None
0.980 and 0.963
Full-matrix least-squares on F ²
4109 / 1 / 232
0.990
R1 = 0.0493, WR2 = 0.0939
R1 = 0.1168, WR2 = 0.1161
0.15 and -0.15 e.A ⁻³
0.01(10)

VII. Grinding-fuming cycles of the luminophores



Figure S27. Photographs of a) $TPE(TIPS)_4$ and b) $TPE(TMS)_4$ showing colour change that is visible to naked eye under day light before and after grinding







Figure S29. Emission spectra of as prepared, fumed and ground samples of a&b) TPE(TIPS)₄ c&d) TPE(TMS)₄



Figure S30. CIE chromaticity diagram of as prepared and ground samples of $TPE(TIPS)_4$ (a&b) and $TPE(TIPS)_4$ (c&d).

VIII. Time resolved fluorescence measurements



Figure S31. Time resolved fluorescence decay profile of TPE(TIPS)₄ in as prepared and ground forms.



Figure S32. Time resolved fluorescence decay profile of TPE(TMS)₄ in as prepared and ground forms.

IX. Absorption and emission spectra of intermediates



Figure S33. UV-Visible absorption spectra of a) TPE and b) TPE-I₄ before and after grinding in the solid state



Figure S34. Emission spectra of a) TPE and b) TPE-I₄ before and after grinding in the solid state

X. IR and Raman analysis



Figure S35. IR spectra of as prepared, ground and fumed samples of a) $TPE(TIPS)_4$ and b) $TPE(TMS)_4$



Figure S36. Raman spectrum of as prepared TPE(TIPS)₄



Figure S38. Raman spectrum of as prepared TPE(TMS)₄



Figure S39. Raman spectrum of ground TPE(TMS)₄

XI. Photographs of single crystals of the luminophores



Figure 40. Photographs of crystals of a) TPE(TMS)₄ and b) TPE(TIPS)₄. Crystals of TPE(TIPS)₄ show many cracks in them.

XII. Dihedral angle measured from single crystal data



Figure 41. Dihedral angle between olefinic plane and the benzene rings represented as 1 and 1' of TPE(TMS)₄



Figure S42. Dihedral angle between olefinic plane and the benzene rings represented as 2 and 2' of $TPE(TMS)_4$

XIII. Packing diagram of TPE(TMS)₄ showing the voids



Figure S43. Crystal packing of TPE(TMS)₄ showing small voids (indicated by arrows)

XIV. Powder XRD patterns of the luminophores



Figure S44. PXRD patterns of as prepared, ground, fumed and annealed samples of a) $\mbox{TPE}(\mbox{TIPS})_4$ and b) $\mbox{TPE}(\mbox{TMS})_4$

XV. CP-MASS 13C NMR spectra of the luminophores before and after grinding



Figure S46. Expansion of solid state ¹³C NMR spectrum of as prepared TPE(TIPS)₄



Figure S48. Expansion of solid state ¹³C NMR spectrum of ground TPE(TIPS)₄



Figure S50. Expansion of solid state ¹³C NMR spectrum of fumed TPE(TIPS)₄



Figure S51. Comparison of solid state ¹³C NMR spectra of as prepared, ground and fumed TPE(TIPS)₄



Figure S52. Expansion of comparison of solid state ¹³C NMR spectra of as prepared, ground and fumed TPE(TIPS)₄



Figure S53. Solid state ¹³C NMR spectrum of as prepared TPE(TMS)₄



Figure S54. Expansion of solid state ¹³C NMR spectrum of as prepared TPE(TMS)₄



Figure S55. Solid state ¹³C NMR spectrum of ground TPE(TMS)₄



Figure S56. Expansion of solid state ¹³C NMR spectrum of ground TPE(TMS)₄



Figure S57. Solid state ¹³C NMR spectrum of fumed TPE(TMS)₄



Figure S58. Expansion of solid state ¹³C NMR spectrum of fumed TPE(TMS)₄



Figure S59. Comparison of solid state ¹³C NMR spectra of as prepared, ground and fumed TPE(TMS)₄



Figure S60. Expansion of comparison of solid state ¹³C NMR spectra of as prepared, ground and fumed TPE(TMS)₄

XVI. Variable temperature NMR spectra of TPE(TIPS)₄

The temperature range used for the analysis was 25 °C to -40 °C in three cycles, i.e., 25 °C to -40 °C (cooling), then -40 °C to 25 °C (heating) and finally 25 °C to -40 °C (cooling). In ¹H NMR, the two doublets at 7.238 ppm and 6.923 ppm shifted slightly upfield when the temperature was lowered from 25 °C to -40 °C; when the temperature is increased from -40 °C to 25 °C they shift back to downfield; finally when the temperature was lowered again from 25 °C to -40 °C, the doublets shifted upfield. Similarly, upfield shift from 143.285 ppm (for olefinic carbon) and 140.799 ppm (for aromatic carbon attached directly to olefin) to 143.082 ppm and 140.308 ppm, respectively was observed when the temperature was lowered from 25 °C to -40 °C. These peaks were found to shift downfield and upfield when the temperature of the experiment was varied from -40 °C to 25 °C and from 25 °C to -40 °C, respectively (Figure S62-S67, supporting information).



Figure S61. VT ¹H NMR of TPE(TIPS)₄ from 25 °C to -40 °C



Figure S62. Expansion of VT ¹H NMR of TPE(TIPS)₄ from 25 °C to -40 °C



Figure S63. VT ¹H NMR of TPE(TIPS)₄ from -40 °C to 25 °C



Figure S64. Expansion of VT ¹H NMR of TPE(TIPS)₄ from -40 °C to 25 °C



Figure S65. VT ¹H NMR of TPE(TIPS)₄ from 25 °C to -40 °C



Figure S66. Expansion of VT ¹H NMR of TPE(TIPS)₄ from 25 °C to -40 °C

XVII. NMR spectra showing the stability of the luminophore towards grinding



Figure S67. ¹H NMR spectra of as prepared (below) and ground (above) samples of $TPE(TMS)_4$ in $CDCl_3$

XVIII. SEM, TEM and Fluorescence microscope images



Figure S68. SEM images of as prepared TPE(TIPS)₄ sample before (a) and (b) after crystallization. e&f) ground and fumed samples. c&g) fluorescence microscope images of the crystals. d&h) TEM images of as prepared (top right panel) and ground (bottom right panel) samples.



Figure S69. SEM images of as prepared TPE(TMS)₄ sample before (a) and (b) after crystallization. e&f) ground and fumed samples. c&g) fluorescence microscope images of the crystals. d&h) TEM images of as prepared (top right panel) and ground (bottom right panel) samples.

XIX. Thermal data of the luminophores



Figure S70. Thermal gravimetric traces of TPE(TIPS)₄ and TPE(TMS)₄



Figure S71. DSC of as prepared sample of TPE(TIPS)₄



Figure S72. Expansion of DSC of as prepared sample of TPE(TIPS)₄



Figure S73. DSC of ground sample of TPE(TIPS)₄



Figure S74. Expansion of DSC of ground sample of TPE(TIPS)₄



Figure S75. DSC of as prepared sample of TPE(TMS)₄



Figure S76. DSC of ground sample of TPE(TMS)₄



Figure S77. Expansion of DSC of ground sample of TPE(TMS)₄

XX. Computational data of the luminophores



Figure S78. Frontier molecular orbitals of TPE(TIPS)₄ and TPE(TMS)₄.



HOMO-LUMO Gap = 3.44 eV

Figure S79. Frontier orbitals along with other higher and lower energy orbitals of TPE(TIPS)_{4.}



HOMO-LUMO Gap = 3.44 eV

Figure S80. Frontier orbitals along with other higher and lower energy orbitals of TPE(TMS)₄.



Figure S81. Calculated absorption spectrum of TPE(TIPS)₄ using TDDFT calculation.



Figure S82. Calculated absorption spectrum of TPE(TMS)₄ using TDDFT calculation.

Table S1. TD-DFT calculated electronic transition configurations for **1**, **[TPE (TIPS)**₄] and **2**, **[TPE (TMS)**₄] along with their corresponding excitation energies and oscillator strengths.^[a]

Transition Configuration	Excitation Energy	Excitation wavelength	Oscillator strength
	(eV)	(nm)	
HOMO->LUMO (100%)	3.03	408.6	0.7887
H-2->LUMO (16%)		336.7	0.2913
HOMO->L+1 (83%)	3.68		
H-1->LUMO (48%)		332.8	0.0003
HOMO->L+2 (51%)	3.72		
H-1->LUMO (50%)		328.1	0.0261
HOMO->L+2 (47%)	3.77		
H-2->LUMO (82%)		318.5	1.5342
HOMO->L+1 (16%)	3.89		
H-3->LUMO (86%)		312.8	0.0054
HOMO->L+3 (11%)	3.96		
H-10->LUMO (11%)		293.1	0.006
HOMO->L+4 (77%)	4.23		
H-8->LUMO (77%)		286.5	0.0005
HOMO->L+6 (14%)	4.32		
HOMO->L+3 (72%)	4.34	285.2	0.0004
H-5->LUMO (37%)		280.9	0.0016
H-4->LUMO (44%)	4.41		
H-5->LUMO (43%)		280.9	0.0008

TPE (TIPS)₄

H-4->LUMO (37%)	4.41		
H-6->LUMO (80%)	4.42	280.5	0.0001
H-7->LUMO (79%)	4.43	280.0	0.0026
H-12->LUMO (18%)		278.7	0.0121
HOMO->L+5 (61%)	4.44		
H-11->LUMO (49%)		278.6	0.0006
H-10->LUMO (19%)	4.45		
H-11->LUMO (21%)		271.8	0.0173
H-10->LUMO (55%)	4.45		
HOMO->L+4 (16%)			
H-2->L+1 (10%)		269.4	0.4912
H-1->L+2 (76%)	4.60		
H-2->L+1 (21%)		267.3	0.0551
H-1->L+1 (60%)	4.63		
H-9->LUMO (23%)		266.8	0.0873
H-2->L+1 (48%)	4.64		
H-1->L+1 (13%)			
H-9->LUMO (69%)	4.66	266.0	0.0024
H-2->L+1 (16%)			
H-3->L+1 (93%)	4.69	264.3	0.01
H-8->LUMO (11%)		262.4	0.0007
HOMO->L+6 (73%)	4.72		
H-12->LUMO (44%)		262.3	0.0956
H-3->L+2 (20%)			
HOMO->L+5 (19%)	4.72		
H-3->L+2 (10%)	4.78	259.1	0.0447
H-2->L+2 (53%)			
H-3->L+2 (65%)	4.78	259.0	0.1684
H-11->LUMO (10%)		256.3	0.0002
H-2->L+2 (10%)	4.83		
HOMO->L+7 (60%)			
H-13->LUMO (71%)		251.6	0.0246
H-12->LUMO (18%)	4.92		
H-14->LUMO (80%)	4.95	250.8	0.0293
H-17->LUMO (16%)		248.1	0.0007
H-4->LUMO (16%)			
H-4->L+1 (29%)	4.99		
H-4->L+2 (14%)			
H-15->LUMO (22%)		247.7	0.0
H-5->LUMO (11%)			
H-5->L+1 (13%)	5.00		
H-5->L+2 (15%)			

Table S1. TD-DFT calculated electronic transition configurations for **1**, **[TPE (TIPS)**₄] and **2**, **[TPE (TMS)**₄] along with their corresponding excitation energies and oscillator strengths.^[a]continued

Transition Configuration	Excitation Energy	Excitation wavelength	Oscillator strength
C C	(eV)	(nm)	C C
HOMO->LUMO (100%)	3.04	406.7	0.7338
H-2->LUMO (16%)			
HOMO->L+1 (83%)	3.69	335.9	0.2716
H-1->LUMO (35%)			
HOMO->L+2 (64%)	3.73	332.0	0.0001
H-1->LUMO (63%)			
HOMO->L+2 (34%)	3.80	325.5	0.0259
H-2->LUMO (83%)			
HOMO->L+1 (15%)	3.94	314.7	1.4043
H-3->LUMO (83%)			
HOMO->L+3 (14%)	3.99	310.5	0.0
H-6->LUMO (16%)			
HOMO->L+4 (77%)	4.23	292.6	0.0069
H-4->LUMO (79%)			
HOMO->L+6 (13%)	4.32	286.7	0.0007
HOMO->L+3 (68%)	4.35	284.8	0.0
H-11->LUMO (27%)			
HOMO->L+5 (62%)	4.45	278.5	0.0148
H-5->LUMO (71%)	4.45	278.1	0.0
H-7->LUMO (77%)	4.54	272.8	0.0043
H-10->LUMO (24%)			
H-8->LUMO (42%)	4.54	272.6	0.0016
H-10->LUMO (30%)			
H-9->LUMO (11%)	4.54	272.6	0.0003
H-8->LUMO (35%)			
H-10->LUMO (21%)			
H-9->LUMO (57%)	4.55	272.5	0.0001
H-6->LUMO (75%)			
HOMO->L+4 (16%)	4.57	271.2	0.0184
H-1->L+2 (82%)	4.63	267.3	0.3162
H-2->L+2 (19%)			
H-1->L+1 (69%)	4.67	265.1	0.0001
H-2->L+1 (92%)	4.68	264.6	0.2801
H-11->LUMO (63%)	4.73		
HOMO->L+5 (24%)		262.0	0.0508
H-1->L+2 (13%)			
HOMO->L+6 (70%)	4.73	261.9	0.0004
H-3->L+1 (95%)	4.74	261.5	0.0075
H-3->L+2 (89%)	4.82	256.8	0.2542
H-12->LUMO (87%)	4.83	256.5	0.0023
H-5->LUMO (15%)			
HOMO->L+7 (66%)	4.83	2.55.9	0.0

TPE (TMS)₄

H-2->L+2 (68%)			
H-1->L+1 (10%)	4.87	254.6	0.0012
H-4->L+1 (43%)			0.0043
H-3->L+4 (19%)	5.10	242.7	
H-6->L+1 (23%)			
H-2->L+4 (37%)			
H-1->L+5 (11%)	5.14	241.2	0.0001
HOMO->L+7 (12%)			
H-11->L+1 (11%)			
H-6->L+2 (13%)		241.1	
H-1->L+4 (51%)	5.14		0.0001
H-5->L+1 (21%)			
H-4->L+2 (40%)	5.16	240.0	0.0288
H-1->L+6 (11%)			

[a]: Only the transitions with equal or greater than 10 % contribution are listed here.



Figure S83. Graph of ΔE vs dihedral angle of TPE(TIPS)₄



Figure S84. Graph of ΔE vs dihedral angle of TPE(TMS)₄





Figure S85. Structures of TPE(TIPS)₄ obtained by freezing the coordinates at various dihedral angle with the corresponding energy in hartree.



 $\Phi = 20^{\circ}$ E_h = -2941.657495



 $\Phi = 25^{\circ}$ E_h = -2941.846841



 $\Phi = 30^{\circ}$ E_h = -2941.962366



 $\Phi = 35^{\circ}$ E_h = -2942.030194



 $\Phi = 40^{\circ}$ E_h = -2942.067467



 $\Phi = 50^{\circ}$ E_h = -2942.095431



 $\Phi = 45^{\circ}$ E_h = -2942.086471



 $\Phi = 55^{\circ}$ E_h = -2942.099294



 $\Phi = 60^{\circ}$ E_h = -2942.100291



 $\Phi = 65^{\circ}$ E_h = -2942.099724



 $\Phi = 70^{\circ}$ E_h = -2942.098417



 $\Phi = 75^{\circ}$ E_h = -2942.096972



Figure S86. Structures of TPE(TMS)₄ obtained by freezing the coordinates at various dihedral angle with the corresponding energy in hartree.

XXI. Writing-erasing sequence on a filter paper impregnated with a solution of TPE(TMS)₄ in DCM



Figure S87. Photographs of impressions/solvent vapor erasing made on a filter paper, impregnated with a solution of TPE(TMS)₄ DCM, taken under UV light (365 nm)



XXII. Photographs of pelletizer and the pellets made at different pressure

Figure S88. Pelletizer used for making the pellets under various pressures.



Figure S89. Photographs of TPE(TIPS)₄ showing the color change upon increasing the pressure: under day light (top) and UV light (bottom, 365 nm excitation)



Figure S90. Photographs of TPE(TMS)₄ showing the color change upon increasing the pressure: under day light (top) and UV light (bottom, 365 nm excitation)

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