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Supporting Information

Ultralong Room Temperature Phosphorescence and Ultraviolet Fluorescence From a Simple TriarylPhosphine Oxides

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1. General experimental procedures

1.1. Materials

The chemicals were purchased from commercial suppliers (Avra Scientific, India; Spectrochem, India; Merck, Germany) and used as received unless otherwise mentioned. The Standard Schlenk-line technique was used for reactions. THF was dried over sodium and distilled out under a nitrogen atmosphere.

1.2. Methods

¹H, ³¹P, ¹³C spectra were recorded at 25 °C on a Bruker Avance 500 MHz NMR Spectrometer operating at a frequency of 500 MHz for ¹H and, 201 MHz for ³¹P and 125 MHz for ¹³C. ¹H NMR spectra were referenced to TMS (0.00 ppm) as an internal standard. Chemical shift multiplicities are reported as singlet (s), doublet (d), triplet (t), quartet (q), and multiplet (m). ³¹P NMR chemical shift values were referenced to the external standard phosphorous signal of 85% H₃PO₄. High-resolution mass spectra (HRMS) were recorded on a Micromass Q-ToF High-Resolution Mass Spectrometer by electrospray ionization (ESI) method. Elemental analysis data were recorded in a C, H, N, S analyzer manufactured by Thermoscientific. Electronic absorption spectra, fluorescence emission spectra and time-resolved fluorescence (TRF) decay measurements were recorded on a SHIMADAZU UV-2600 spectrophotometer and FLS-980 EDINBURGH spectrometer, respectively. Time gated emission spectra were recorded using the same FLS 980 fluorimeters by excitation source of pulsed microsecond flash lamp (μ F1) with a pulse width of 1.1 μ s. Temperature-dependent emission studies were also performed using the same instrument with the help of an OXFORD cryostat. Solutions of all the compounds for spectral measurements were prepared using anhydrous spectrophotometric grade solvents and standard volumetric glasswares. Quartz cuvettes with sealing screw caps were used for the solution state spectral measurements. Single crystal X-ray diffraction studies were carried out with a Bruker SMART APEX diffractometer at 90 K equipped with 4-axis goniometer for all the compounds. The structures were solved by direct methods and refined by full-matrix least-squares on F 2 using SHELXTL software. Density functional theory (DFT) calculations were done using B3LYP functional with 6-311++G(d,p)/6-311G(d,p) basis sets as incorporated in Gaussian 09 package for all the atoms.^[1,2] The optimized structures and the frontier molecular orbitals (FMOs) were viewed using Gaussview5.0.

2. Synthesis details

2.1. Synthesis Procedures

Synthesis of Triphenylphosphine (1)

Analytically pure triphenylphosphine crystals were obtained by repeated recrystallization of commercially available triphenylphosphine from hexane and dichloromethane mixture (4:1). ¹H NMR (500 MHz, DMSO-d⁶): $\delta_{\rm H}$ (ppm): 7.41-7.39 (m, 9 H), 7.25-7.23 (m, 6H). ¹³C NMR (125 MHz, CDCl₃) $\delta_{\rm C}$ (ppm): 137.26, 137.18, 133.94, 133.87, 133.79, 133.64, 128.83, 128.79, 128.68, 128.64, 128.58, 128.49, 128.45. ³¹P NMR (201 MHz, DMSO-d⁶): $\delta_{\rm P}$ (ppm): -6.67. HRMS (ESI-TOF): (*m/z*) calcd for C₁₈H₁₅PH [M+H]⁺: 263.0990; Found: 263.0990. Elemental analysis (%) for C₁₈H₁₅P: C 82.43, H 5.76; found: C 82.56, H 5.63.

Synthesis of Triorthotolylphosphine (2)

Analytically pure triorthotolylphosphine crystals were obtained by repeated recrystallization from hexane and dichloromethane mixture (4:1). ¹H NMR (500 MHz, CDCl₃): $\delta_{\rm H}$ (ppm): 7.29-7.24 (6H, m), 7.12-7.08 (3H, m), 6.77-6.74 (3H, m), 2.42 (9H, s). ¹³C NMR (125 MHz, CDCl₃) $\delta_{\rm C}$ (ppm): 142.86, 142.65, 134.51, 134.42, 133.08, 130.11, 128.70, 126.18, 21.31, 21.14. ³¹P NMR (201 MHz, CDCl₃): $\delta_{\rm P}$ (ppm): -29.47. HRMS (ESI-TOF): (*m/z*) calcd for C₂₁H₂₁PH [M+H]⁺: 305.1459; Found: 305.1457. Elemental analysis (%) for C₂₁H₂₁P: C 82.87, H 6.95; found: C 82.95, H 6.78.

Synthesis of Trixylylphosphine (3)

2-Bromo-meta-xylene (8.33 g, 45.01 mmol) was added dropwise to a slurry of magnesium turnings (1.02 g, 42.00 mmol in 100 mL THF) in a predried 250 mL RB at 25 °C under stirring conditions. The resultant reaction mixture was refluxed for 6 hours, and then the reaction temperature was brought down to -78 °C, and PCl₃ (1.73 g, 12.61 mmol) was added dropwise under stirring conditions. After 30 minutes of stirring at -78 °C, the reaction temperature was raised to 25 °C, and the stirring was continued for another 12 h. The reaction mixture was washed with brine solutions and extracted with dichloromethane. The combined dichloromethane solutions were stored over anhydrous MgSO₄. Removal of all the organic volatiles under reduced pressure gave the crude product. Analatically pure compound was obtained after silica gel column chromatography purification using hexane and ethyl acetate (95:5) as eluent. Single crystals of **3** were obtained by repeated recrystallization from dichloromethane and hexane (1:4) solutions. Yield. 2.3 g, (44.23%). ¹H NMR (500 MHz,

CDCl₃): $\delta_{\rm H}$ (ppm): 7.10 (3H, t, J = 8.0 Hz), 6.97-6.95 (6H, m), 2.09 (18H, s). ¹³C NMR (125 MHz, CDCl₃) $\delta_{\rm C}$ (ppm): 143.33, 143.15, 135.35, 135.16, 129.28, 128.52, 23.38, 23.22. ³¹P NMR (201 MHz, CDCl₃): $\delta_{\rm P}$ (ppm): -34.31. HRMS (ESI-TOF): (*m/z*) calcd for C₂₄H₂₈P [M+H]⁺: 347.1929; Found: 347.1928. Elemental analysis (%) for C₂₄H₂₇P: C 83.20, H 7.86; found: C 83.35, H 7.71.

Synthesis of Trimesitylphosphine (4)

Compound **4** was synthesised following the procedure used for the preparation of **3**. The quantities involved and characterization data are as follows. Magnesium (1.02 g, 42.00 mmol), 2-Bromomesitylene (8.33 g, 45.01 mmol) and PCl₃ (1.73 g, 12.61 mmol). Analytically pure compound was obtained by recrystallization from dichloromethane and hexane (1:4) solutions. Yield. 3.2 g, (41%). ¹H NMR (500 MHz, CDCl₃): $\delta_{\rm H}$ (ppm): 6.79 (6H, s), 2.26-2.05 (27H, m). ¹³C NMR (125 MHz, CDCl₃) $\delta_{\rm C}$ (ppm): 143.18, 143.00, 137.93, 132.12, 131.94, 130.11, 23.25, 23.08, 21.37. ³¹P NMR (201 MHz, CDCl₃): $\delta_{\rm P}$ (ppm): -36.29. HRMS (ESI-TOF): (*m/z*) calcd. for C₂₇H₃₄P [M+H]⁺: 389.2398; Found: 389.2397. Elemental analysis (%) for C₂₇H₃₃P: C 83.47, H 8.56; found: C 83.51, H 8.54.

Synthesis of Triphenylphosphine oxide (5)

H₂O₂ (30 % solutions, 5 mL) was added to dichloromethane (70 mL) solutions of triphenylphosphine (1 g, 3.81 mmol) at 0 °C under stirring conditions. The resultant reaction mixture was stirred for an additional three hours at the same temperature. Then the reaction mixture was washed with brine solution, and the compound was extracted using dichloromethane and stored over anhydrous MgSO₄. Removal of all the organic volatiles under reduced pressure gave the crude product. Analytically pure triphenylphosphine oxide crystals were obtained by repeated recrystallization from hexane and dichloromethane mixture (4:1). Yield. 0.75 g (71%). ¹H NMR (500 MHz, CDCl₃): $\delta_{\rm H}$ (ppm): 7.70-7.64 (6H, m), 7.56-7.52 (3H, m), 7.48-7.44 (6H, m). ¹³C NMR (125 MHz, CDCl₃) $\delta_{\rm C}$ (ppm): 132.92, 132.14, 132.07, 131.96, 131.94, 128.56, 128.46. ³¹P NMR (201 MHz, CDCl₃): $\delta_{\rm P}$ (ppm): 29.14. HRMS (ESI-TOF): (*m/z*) calcd for C₁₈H₁₆PO [M+H]⁺: 279.0939; Found: 279.0937. Elemental analysis (%) for C₁₈H₁₅OP: C 77.69, H 5.43; found: C 77.54, H 5.30.

Synthesis of Triorthotolylphosphine oxide (6)

Triorthotolylphosphine oxide was prepared following the procedure used for the preparation of **5**. The quantities involved and characterization data are as follows. Triorthotolylphosphine

(1 g, 3.60 mmol) H₂O₂ (30 %, 5 mL). Yield. 0.76 g (65%). ¹H NMR (500 MHz, CDCl₃): $\delta_{\rm H}$ (ppm): 7.44-7.41 (3H, m), 7.32-7.30 (3H, m), 7.16-7.13 (3H, m), 7.11-7.07 (3H, m), 2.49 (9H, s). ¹³C NMR (125 MHz, CDCl₃) $\delta_{\rm C}$ (ppm): 143.54, 143.48, 132.95, 132.85, 132.05, 131.97, 131.85, 131.83, 131.03, 130.23, 125.54, 125.44, 22.01, 21.98. ³¹P NMR (201 MHz, CDCl₃): $\delta_{\rm P}$ (ppm): 37.21. HRMS (ESI-TOF): (*m/z*) calcd for C₂₁H₂₂PO [M+H]⁺: 321.1408; Found: 321.1406. Elemental analysis (%) for C₂₁H₂₁OP: C 78.81, H 6.39; found: C 78.73, H 6.61.

Synthesis of Trixylylphosphine oxide (7)

Compound 7 was prepared following the procedure used for the preparation of 5. The quantities involved and characterization data are as follows. Trixylylphosphine (1 g, 3.60 mmol) and H_2O_2 (30 % solution, 5 mL). Analytically pure compound was obtained by recrystallization from dichloromethane and hexane (1:4) solutions. Yield. 0.68 g (64%). ¹H NMR (500 MHz, CDCl₃): $\delta_{\rm H}$ (ppm): 7.25 (3H, m), 7.01 (6H, s), 2.25 (18H, broad). ¹³C NMR (125 MHz, CDCl₃) $\delta_{\rm C}$ (ppm): 145.65, 139.58, 135.45, 134.71, 130.89, 130.49, 23.77. ³¹P NMR (201 MHz, CDCl₃): $\delta_{\rm P}$ (ppm): 27.32. HRMS (ESI-TOF): (*m/z*) calcd for C₂₄H₂₈PO [M+H]⁺: 363.1878; Found: 363.1875. Elemental analysis (%) for C₂₄H₂₇OP: C 79.39, H 7.31; found: C 79.53, H 7.51.

Synthesis of Trimesitylphosphine oxide (8)

Compound **8** was prepared following the procedure used for the preparation of **5**. The quantities involved and characterization data are as follows. Trixylylphosphine (1 g, 3.60 mmol) and H_2O_2 (30 % solution, 5 mL). Analytically pure compound was obtained by recrystallization from dichloromethane and hexane (1:4) solutions. Yield. 0.59 g (57%). ¹H NMR (500 MHz, CDCl₃): $\delta_{\rm H}$ (ppm): 6.83 (6H, s), 2.64-1.90 (27H, broad). ¹³C NMR (125 MHz, CDCl₃) $\delta_{\rm C}$ (ppm): 145.57, 140.71, 140.69, 139.59, 132.53, 131.77, 131.20, 23.64, 21.06, 20.98. ³¹P NMR (201 MHz, CDCl₃): $\delta_{\rm P}$ (ppm): 27.15. HRMS (ESI-TOF): (*m/z*) calcd for C₂₇H₃₄PO [M+H]⁺: 405.2347; Found: 405.2351. Elemental analysis (%) for C₂₇H₃₃OP: C 80.05, H 8.11; found: C 80.17, H 8.22.

3. Structural characterizations



Figure S1. ¹H NMR spectrum of 1 in DMSO-d⁶.



Figure S2.³¹P NMR spectrum of 1 in DMSO-d⁶.



Figure S3. ³¹P NMR spectrum of 1 in THF-d⁸ recorded at different temperatures.



Figure S4. ¹³C NMR spectrum of 1 in CDCl₃.



Figure S6. ³¹P NMR spectrum of 2 in CDCl₃.



Figure S7. ¹³C NMR spectrum of 2 in CDCl₃.



Figure S8. ¹H NMR spectrum of 3 in CDCl₃.



Figure S10. ¹³C NMR spectrum of 3 in CDCl₃.



Figure S11. ¹H NMR spectrum of 4 in CDCl₃.



Figure S12. ³¹P NMR spectrum of 4 in CDCl₃.



Figure S14. ¹H NMR spectrum of 5 in CDCl₃.



Figure S15. ³¹P NMR spectrum of 5 in CDCl₃.



Figure S16. ¹³C NMR spectrum of 5 in CDCl₃.



Figure S18. ³¹P NMR spectrum of 6 in CDCl₃.



Figure S19. ¹³C NMR spectrum of 6 in CDCl₃.



Figure S20. ¹H NMR spectrum of **7** in CDCl₃. ((Due to fluxional behavior of compound **7**, broad ¹H NMR signals are observed in upfield region 2.70-1.70 ppm).



Figure S21. ¹H NMR spectrum of **7** in CDCl₃ recorded at different temperatures (One broad peak in aromatic region splits into two peaks as temperature goes down and also two broad peaks in aliphatic region become sharp at low temperature).



Figure S22. ³¹P NMR spectrum of 7 in CDCl₃.



Figure S24. ¹H NMR spectrum of **8** in CDCl₃. (Due to fluxional behavior of compound **8**, broad ¹H NMR signals are observed in upfield region at 2.64-1.90 ppm).



Figure S25. ³¹P NMR spectrum of 8 in CDCl₃.



Figure S26. ¹³C NMR spectrum of 8 in CDCl₃.

High Resolution Mass Spectral (HRMS) Characterization



Figure S27. HRMS of compound 1.



Figure S28. HRMS of compound 2.



Figure S29. HRMS of compound 3.



Figure S30. HRMS of compound 4.



Figure S31. HRMS of compound 5.



Figure S32. HRMS of compound 6.



Figure S33. HRMS of compound 7.



Figure S34. HRMS of compound 8.

4. Single crystal X-ray diffraction data

Table S1. Bond lengths and dihedral angle between phenyl ring measured from cr	rystal
structures	

Compound	P-C bond length (Å)	Dihedral angle (deg)	P=O bond length (Å)
1	1.827, 1.828, 1.829	83.80, 78.36, 74.83	-
2	1.835, 1.835, 1.836	84.71, 84.06, 75.65	-
3	1.834, 1.836, 1.839	89.11, 81.33, 72.10	-
5	1.799, 1.803, 1.807	82.43, 80.22, 76.94	1.486
6	1.811, 1.812, 1.820	89.39, 78.86, 75.85	1.477
7	1.828, 1.834, 1.835	85.05, 77.91, 71.95	1.489
8	1.830, 1.832, 1.838	72.20, 74.33, 85.68	1.491

Compound	1	5	7	8
Empirical	C ₁₈ H ₁₅ P	C ₁₈ H ₁₅ PO	C ₂₄ H ₂₇ PO	C ₂₇ H ₃₃ PO
formula				
FW	262.27	278.27	362.42	404.5
T (K)	90(2) K	90(2) K	90(2) K	90(2) K
Crystal system	Monoclinic	Orthorhombic	Orthorhombic	Triclinic
Space group	$P2_l/c$	Pbca	Pbca	P-1
a/Å	8.3927(5)	9.0608(2)	14.5808(7)	8.081(5)
b/Å	14.7980(8)	11.0774(2)	8.1047(4)	16.167(10)
c/Å	11.2534(6)	28.8009(6)	32.6131(15)	18.509(12)
α/deg	90	90	90	105.941(4)
β/deg	91.584(3)	90	90	98.394(4)
γ/deg	90	90	90	99.524(4)
V/Å ³	1397.08(13)	2890.75(10)	3854.0(3)	2246.01(3)
Z	4	8	8	4
$\rho_{calcd} (gcm^{-3})$	1.247	1.279	1.249	1.196
μ (Μο Κα)	0.179	0.182	0.153	0.138
(mm ⁻¹)				
λ/Å	0.71073	0.71073	0.71073	0.71073
F (000)	552	1168	1552	872
Collected reflns	31002	19821	56137	27904
Unique reflns	4273	3464	5879	7127
GOF (F2)	1.070	1.035	1.083	1.155
R1 [I>2σ(I)] ^[a]	0.0335	0.0386	0.0398	0.0898
wR2 [I>2σ(I)] ^[b]	0.0928	0.1011	0.1424	0.2192
CCDC Number	2076607	2076602	2076604	2076655

Table S2. Crystallographic data and refinement parameters

 $[a] R1 = \Sigma | |Fo| - |Fc| | / \Sigma |Fo|. [b] wR2 = [\Sigma \{w(Fo 2 - Fc 2) 2\} / \Sigma \{w(Fo 2) | Fo| \} /$

Compound	2	2 (Reported) ^[3]	3	3 (Reported) ^[4]
Empirical	$C_{21}H_{21}P$	C ₂₁ H ₂₁ P	C ₂₄ H ₂₇ P	C ₂₄ H ₂₇ P
formula				
FW	304.35	304.35	347.20	347.20
T (K)	90(2) K	295 K	90(2) K	295 K
Crystal system	Triclinic	Triclinic	Monoclinic	Monoclinic
Space group	P-1	P-1	C2/c	B 1 1 2/b
a/Å	10.8081(4)	12.081(5)	29.6762(16)	30.20(1)
b/Å	11.8962(5)	10.915(5)	8.2001(4)	16.34(1)
c/Å	14.0291(5)	14.348(7)	16.1763(9)	8.305(3)
α/deg	109.752(2)	91.95(5)	90	90
β/deg	92.811(2)	110.58(4)	103.810(3)	90
γ/deg	97.859(2)	98.22(5)	90	103.47(4)
V/Å ³	1672.92(11)	1745.78	3822.7(4)	3985.52
Z	4	4	8	8
$\rho_{calcd} (gcm^{-3})$	1.208	1.158	1.109	
μ (Μο Κα)	0.159		0.144	
(mm ⁻¹)				
λ/Å	0.71073		0.71073	
F (000)	648		1272.0	
Collected reflns	30433		38784	
Unique reflns	10041		5847	
GOF (F2)	1.027		2.625	
R1 [I>2σ(I)] ^[a]	0.0525		0.0667	
wR2 [I>2σ(I)] ^[b]	0.1638		0.2944	
CCDC Number	2077851		2077058	

Table S3. Crystallographic data and refinement parameters

 $[a] R1 = \Sigma | |Fo| - |Fc| | / \Sigma |Fo|. [b] wR2 = [\Sigma \{w(Fo 2 - Fc 2) 2\} / \Sigma \{w(Fo 2) | Fo| \} /$

Compound	4	4 (Reported) ^[5]	6	6 (Reported) ^[3]
Empirical	C ₂₇ H ₃₃ P	C ₂₇ H ₃₃ P	C ₂₁ H ₂₁ PO	C ₂₁ H ₂₁ PO
formula				
FW	389.51	389.51	320.35	320.35
T (K)	90(2) K	295 K	90(2) K	295 K
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	C2/c	C_C	$P2_{1}/c$	$P2_{I}/c$
a/Å	11.3108(9)	11.390(5)	16.1067(19)	9.039(5)
b/Å	11.8978(9)	12.034(4)	7.8044(9)	17.282(6)
c/Å	17.1822(13)	17.564(9)	14.5026(16)	35.192(12)
α/deg	90	90	90	90
β/deg	105.240(4)	104.22(4)	101.468(6)	95.12(1)
γ/deg	90	90	90	90
V/Å ³	2231.0(3)	2333.68	1786.6(4)	5475.48
Z	4	4	4	4
$\rho_{calcd} (gcm^{-3})$	1.160	1.106	1.191	1.249
μ (Μο Κα)	0.133		0.156	
(mm ⁻¹)				
λ/Å	0.71073		0.71073	
F (000)	844.0		680	
Collected reflns	20172		56137	
Unique reflns	3385		5378	
GOF (F2)	1.025		1.074	
R1 [I>2σ(I)] ^[a]	0.1350		0.0648	
wR2 [I>2σ(I)] ^[b]	0.3217		0.2182	
CCDC Number	2077916		2076603	

Table S4. Crystallographic data and refinement parameters

 $[a] R1 = \Sigma | |Fo| - |Fc| | / \Sigma |Fo|. [b] wR2 = [\Sigma \{w(Fo \ 2 - Fc \ 2 \) \ 2 \] / \Sigma \{w(Fo \ 2 \) \] / \Sigma \{w(Fo \ 2 \) \] / \Sigma \{w(Fo \ 2 \) \] / \Sigma \{w(Fo \ 2 \) \] / \Sigma \{w(Fo \ 2 \) \] \} \}$



Figure S35: Intermolecular interactions observed in crystals of 1.



Figure S36: Intermolecular interactions (C-H...pi, (CH₃)C-H...H-C(CH₃), (CH₃)C-H...H-C(phenyl)) observed in crystals of **2**.



Figure S37: Intermolecular H-bonding (left), slipped pi...pi and (phenyl)C-H...pi (right) interactions observed in crystals of 5.



Figure S38: Intermolecular H-bonding (left), and (phenyl)C-H...pi (right) interactions observed in crystals of 6.



Figure S39: Intermolecular H-bonding (left), and (phenyl)C-H...pi (right) interactions observed in crystals of 7 (a, b), **8** (c, d).

5. Photophysical data



Figure S40: UV-Visible absorption spectra of **1** (a) and **2** (b) in different solvents (conc. 10⁻⁵ M).



Figure S41: UV-Visible absorption spectra of **3** (a) and **4** (b) in different solvents (conc. 10⁻⁵ M).



Figure S42: UV-Visible absorption spectra of **5** (a) and **6** (b) in different solvents (conc. 10⁻⁴ M).



Figure S43: UV-Visible absorption spectra of **7** (a) and **8** (b) in different solvents (conc. 10⁻⁴ M).



Figure S44. Photoluminescence spectra of compound 1 (a), 2 (b), and corresponding normalized PL spectra of 1 (c), 2 (d) in different solvents (conc. 10^{-5} M).



Figure S45. Photoluminescence spectra of compound 3 (a), 4 (b), and corresponding normalized PL spectra of 3 (c), 4 (d) in different solvents (conc. 10^{-5} M).



Figure S46: Photoluminescence spectra of 1 (a), 2 (b), 3 (c) and 4 (d) in chloroform with different concentrations.



Figure S47. Excitation spectra of compound 1 monitored at emission wavelengths 290 nm (a), 490 nm (b), in hexane (conc. 10^{-5} M).



Figure S48. Excitation spectra of compound **2** monitored at emission wavelengths 300 nm (a), 470 nm (b), in hexane (conc. 10^{-5} M).



Figure S49. Excitation spectra of compound 3 (a), and 4 (b) monitored at their emission maximum in chloroform (conc. 10^{-5} M).

Compound	Solvent	$\lambda_{max}(UV) (nm)$	ε (10 ⁴)	$\lambda_{max}(PL) (nm)$
			(mol-1 L cm-1)	
1	Hexane	263	1.10	455
	THF	260, 265, 272	0.39, 0.35.0.25	283
	Chloroform	261	0.95	290, 490
	Methanol	261	1.05	283, 495
2	Hexane	277	1.22	300, 441
	THF	272, 279	0.61, 0.62	291, 464
	Chloroform	278	0.92	300, 465
	Methanol	277	0.81	310, 466
3	Hexane	291, 313	0.56, 0.96	484
	THF	291, 313	0.67, 1.10	500
	Chloroform	293, 315	0.66, 1.06	510
	Methanol	291, 311	0.89, 1.31	516
4	Hexane	312	1.08	490
	THF	290, 313	0.69, 1.05	498
	Chloroform	290, 315	0.82, 1.37	500
	Methanol	289, 313	0.69, 1.06	506
5	Hexane	259. 265, 272	0.16, 0.21, 0.18	nd
	Methanol	261, 265, 273	0.11, 0.21, 0.15	
6	Hexane	271, 278	0.35, 0.35	nd
	Methanol	271, 279	0.38, 0.36	
7	Hexane	281, 289	0.33. 0.32	nd
	Methanol	282, 290	0.35, 0.33	
8	Hexane	279, 288	0.33, 0.34	nd
	Methanol	281, 289	0.35, 0.36	

Table S5: UV-Visible absorption maxima and corresponding molar absorption coefficient,fluorescence emission maximum of 1-8 in different solvents under ambient conditions.

	Fluorescence lifetime			Phosphorescence Lifetime (Crystals)		
		Crystals ($\lambda_{ex} = 375 \text{ nm}$)		77 K	298 K	
	Solutions (298 K)	77 K	298 K	$\lambda_{ex} = 340 \text{ nm}$	$\lambda_{ex} = 340 \text{ nm}$	
1	1.33 ns (Hexane)	0.75 ns (59.26%)	0.66 ns (66.35%)	2.53 ms (100%)	5.45 µs (100.00%)	
	* (THF)	5.43 ns (40.74%)	5.74 ns (33.65%)	$(\lambda_{\rm em} = 430 \text{ nm})$	$(\lambda_{\rm em} = 441 \text{ nm})$	
	1.37 ns (Chloform)	$(\lambda_{\rm em} = 430 \text{ nm})$	$(\lambda_{\rm em} = 441 \text{ nm})$			
	1.80 ns (Methanol)					
2	1.05 ns (Hexane)	0.92 ns (72.49%)	0.80 ns (70.60%)	9.74 ms (100.00%)	4.69 μs (100.00%)	
	1.67 ns (THF)	5.84 ns (27.51%)	5.42 ns (29.40%)	$(\lambda_{\rm em} = 476 \text{ nm})$	$(\lambda_{\rm em} = 431 \text{ nm})$	
	1.35 ns (Chloform)	$(\lambda_{\rm em} = 476 \text{ nm})$	$(\lambda_{\rm em} = 431 \text{ nm})$			
	1.56 ns (Methanol)					
3	1.19 ns (Hexane)	0.56 ns (91.89%)	0.35 ns (66.72%)	304.30 µs (29.57%)	4.30 µs (91.22%)	
	0.85 ns (THF)	4.07 ns (8.11%)	4.19 ns (33.28%)	1.27 ms (41.85%)	15.19 μs (8.78%)	
	0.96 ns (Chloform)	$(\lambda_{\rm em} = 478 \text{ nm})$	$(\lambda_{\rm em} = 488 \text{ nm})$	5.45 ms (28.58%)	$(\lambda_{\rm em} = 488 \text{ nm})$	
	1.01 ns (Methanol)			$(\lambda_{\rm em} = 554 \text{ nm})$		
4	1.06 ns (Hexane)	0.45 ns (60.34%)	0.32 ns (47.52%)	2.97 ms (31.09%)	4.33 μs (91.92%)	
	0.80 ns (THF)	4.92 ns (39.66%)	4.88 ns (52.48%)	11.96 ms (68.91%)	14.89 µs (8.08%)	
	0.76 ns (Chloform)	$\lambda_{\rm em} = 467 \ \rm nm$	$(\lambda_{\rm em} = 475 \text{ nm})$	$\lambda_{\rm em} = 580 \ \rm nm$	$(\lambda_{\rm em} = 469 \text{ nm})$	
	0.94 ns (Methanol)					

 Table S6a: Lifetime data (fluorescence and phosphorescence) of compounds 1-4 in solutions and as prepared crystals.

* THF solution of 1 showed emission in very energy region at ~ 283 nm. Hence lifetime couldn't be recoreded.

	Fluorescence lifetime of crystals		Phosphorescence Lifetime of crystals			
	$(\lambda_{ex} = 375 \text{ nm})$		77	298 K		
	77 K	298 K	$\lambda_{ex} = 260 \text{ nm}$	$\lambda_{ex} = 340 \text{ nm}$	$\lambda_{ex} = 340 \text{ nm}$	
5	2.08 ns (41.32%)	1.58 ns (36.94%)	432.77 ms (31.49%)	141.84 ms (58.20%)	80.54 ms (53.23%)	
	7.20 ns (58.68%)	6.47 ns (63.06%)	914.84 ms (68.51%)	685.64 ms (41.80%)	263.94 ms (46.77%)	
	$(\lambda_{\rm em} = 381 \text{ nm})$	$(\lambda_{\rm em} = 378 \text{ nm})$	$(\lambda_{\rm em} = 410 \text{ nm})$	$(\lambda_{\rm em} = 480 \text{ nm})$	$(\lambda_{\rm em} = 482 \text{ nm})$	
6	1.72 ns (50.79%)	2.27 ns (57.02%)	217.49 ms (28.55%)	192.96 ms (43.79%)	51.11 ms (31.96%)	
	7.52 ns (49.21%)	7.87 ns (42.98%)	1.40 s (71.45%)	1.01 s (56.21%)	315.87 ms (68.04%)	
	$(\lambda_{\rm em} = 410 \text{ nm})$	$(\lambda_{\rm em} = 410 \text{ nm})$	$(\lambda_{\rm em} = 425 \text{ nm})$	$(\lambda_{\rm em} = 475 \text{ nm})$	$(\lambda_{\rm em} = 523 \text{ nm})$	
7	3.60 ns (71.06%)	3.00 ns (75.16%)	52.61 ms (37.61%)	40.24 ms (33.09%)		
	12.30 ns (28.94%)	10.85 ns (24.84%)	476.41 ms (62.39%)	453.69 ms (66.91%)	*	
	$(\lambda_{\rm em} = 400 \text{ nm})$	$(\lambda_{\rm em} = 400 \text{ nm})$	$(\lambda_{\rm em} = 455 \text{ nm})$	$(\lambda_{\rm em} = 475 \text{ nm})$		
8	3.61 ns (68.54%)	3.16 ns (70.59%)	46.51 ms (37.57%)	44.98 ms (60.24%)	15.81 ms (60.92%)	
	22.54 ns (31.46%)	19.70 ns (29.41%)	374.27 ms (62.43%)	283.37 ms (39.76%)	69.67 ms (39.08%)	
	$(\lambda_{\rm em} = 415 \text{ nm})$	$(\lambda_{\rm em} = 416 \text{ nm})$	$(\lambda_{\rm em} = 451 \text{ nm})$	$(\lambda_{\rm em} = 461 \text{ nm})$	$(\lambda_{\rm em} = 549 \text{ nm})$	

Table S6b: Lifetime data (fluorescence and phosphorescence) of as prepared crystals of 5-8.

* Phosphorescence life time of as prepared crystals of compound 7 couldn't be obtained it doesn't decay completely even upto 8 sec. Hence the data couldn't be fitted.

Compound	Φ^{PL} (%)	$\tau_{av} (ns)$	$K_r(S^{-1})$	$K_{nr}(S^{-1})$
1	1.39	2.37	0.58x10 ⁷	41.61x10 ⁷
2	1.96	2.16	0.90x10 ⁷	45.39x10 ⁷
3	1.63	2.63	0.61x10 ⁷	37.40x10 ⁷
4	1.13	2.71	0.41x10 ⁷	36.48x10 ⁷
5	0.52	4.66	0.11x10 ⁷	21.26x10 ⁷
6	0.95	4.68	0.20x10 ⁷	21.17x10 ⁷
7	1.01	4.95	0.20x10 ⁷	20.00x10 ⁷
8	0.41	8.02	0.05x10 ⁷	12.42x10 ⁷

Table S7. Absolute PL quantum yield (Φ^{PL}) (%) and radiative (K_r), non-radiative decay

constant (K_{nr}) for as prepared crystals.



Figure S50: PL spectra of as prepared crystals of 1 (a), 2 (b), 3 (c) and 4 (d) with different excitations.



Figure S51: Fluorescence and phosphorescence spectra of as prepared crystals of compounds 1 (a), 2 (b) at 77 and 298 K with 100 μ s delay and $\lambda_{ex} = 340$ nm.



Figure S52: Fluorescence and phosphorescence spectra of as prepared crystals of compounds 3 (a), 4 (b) at 77 and 298 K with 100 μ s delay and $\lambda_{ex} = 340$ nm.



Figure S53: PL spectra of as prepared crystals of 5 with different excitations (a, b).



Figure S54: PL spectra of as prepared crystals of 6 with different excitations (a, b).



Figure S55: PL spectra of as prepared crystals of 7 with different excitations (a, b).



Figure S56: PL spectra of as prepared crystals of 8 with different excitations (a, b).



Figure S57: Fluorescence spectra of as prepared crystals of compounds 1 (a), 2 (b), 3 (c), and 4 (d) at 77 and 298 K, $\lambda_{ex} = 340$ nm.



Figure S58: Fluorescence spectra of as prepared crystals of compounds 5 (a), 6 (b), 7 (c), and 8 (d) at 77 and 298 K, $\lambda_{ex} = 340$ nm.



Figure S59: Phosphorescence lifetime decay profile of as prepared crystals of compound 1 at (a) 77 K ($\lambda_{ex} = 340 \text{ nm}$, $\lambda_{em} = 431 \text{ nm}$, 100 µs delay), and (b) 298 K ($\lambda_{ex} = 340 \text{ nm}$, $\lambda_{em} = 441 \text{ nm}$, 20 µs delay).



Figure S60: Phosphorescence lifetime decay profile of as prepared crystals of compound **2** at (a) 77 K ($\lambda_{ex} = 340 \text{ nm}$, $\lambda_{em} = 478 \text{ nm}$, 100 µs delay), and (b) 298 K ($\lambda_{ex} = 340 \text{ nm}$, $\lambda_{em} = 431 \text{ nm}$, 20 µs delay).



Figure S61: Phosphorescence lifetime decay profile of as prepared crystals of compound **3** at (a) 77 K ($\lambda_{ex} = 340 \text{ nm}$, $\lambda_{em} = 560 \text{ nm}$, 100 µs delay), and (b) 298 K ($\lambda_{ex} = 340 \text{ nm}$, $\lambda_{em} = 488 \text{ nm}$, 20 µs delay).



Figure S62: Phosphorescence lifetime decay profile of as prepared crystals of compound 4 at (a) 77 K ($\lambda_{ex} = 340 \text{ nm}$, $\lambda_{em} = 580 \text{ nm}$, 100 µs delay), and (b) 298 K ($\lambda_{ex} = 340 \text{ nm}$, $\lambda_{em} = 470 \text{ nm}$, 20 µs delay).



Figure S63: Phosphorescence lifetime decay profile of as prepared crystals of compound **5** at (a) 77 K (500 μ s delay) ($\lambda_{ex} = 260$ nm, $\lambda_{em} = 410$ nm and ($\lambda_{ex} = 340$ nm, $\lambda_{em} = 500$ nm)), and (b) 298 K (500 μ s delay), ($\lambda_{ex} = 340$ nm, $\lambda_{em} = 500$ nm).



Figure S64: Phosphorescence lifetime decay profile of as prepared crystals of compound **6** at (c) 77 K (1 ms delay) ($\lambda_{ex} = 260 \text{ nm}$, $\lambda_{em} = 430 \text{ nm}$ and ($\lambda_{ex} = 340 \text{ nm}$, $\lambda_{em} = 480 \text{ nm}$)), and (d) 298 K (1 ms delay), ($\lambda_{ex} = 340 \text{ nm}$, $\lambda_{em} = 520 \text{ nm}$).



Figure S65: Phosphorescence lifetime decay profile of as prepared crystals of compound 7 at (c) 77 K (1 ms delay) ($\lambda_{ex} = 260$ nm, $\lambda_{em} = 475$ nm and ($\lambda_{ex} = 340$ nm, $\lambda_{em} = 480$ nm)), and (d) 298 K (50 µs delay), ($\lambda_{ex} = 340$ nm, $\lambda_{em} = 520$ nm).



Figure S66: Phosphorescence lifetime decay profile of as prepared crystals of compound **8** at (c) 77 K (1 ms delay) ($\lambda_{ex} = 260$ nm, $\lambda_{em} = 450$ nm and ($\lambda_{ex} = 340$ nm, $\lambda_{em} = 480$ nm)), and (d) 298 K (50 µs delay), ($\lambda_{ex} = 340$ nm, $\lambda_{em} = 520$ nm).



Figure S67: Excitation spectra of as prepared crystals of compound 1 (a) and 2 (b).



Figure S68: Excitation spectra of as prepared crystals of compound 3 (a) and 4 (b).



Figure S69: Excitation spectra of as prepared crystals of compound **5** at different emission wavelength (a, b).



Figure S70: Excitation spectra of as prepared crystals of compound 6 at different emission wavelength (a, b).



Figure S71: Excitation spectra of as prepared crystals of compound 7 at different emission wavelength (a, b).



Figure S72: Excitation spectra of as prepared crystals of compound 8 at different emission wavelength (a, b).



Figure S73: Fluorescence and phosphorescence spectra of as prepared crystals of compounds 7, $\lambda_{ex} = 260$ nm (a), $\lambda_{ex} = 340$ nm (b) (Very weak phosphorescence signal is observed at 520 nm for 7 at 298 K, $\lambda_{ex} = 340$ nm).



Figure S74: Fluorescence and phosphorescence spectra of as prepared crystals of compounds **8**, $\lambda_{ex} = 260$ nm (a), $\lambda_{ex} = 340$ nm (b) (Very weak phosphorescence signal is observed at 520 nm for **8** at 298 K, $\lambda_{ex} = 340$ nm).



Figure S75: Phosphorescence spectra of crystals of compound 5 (a), 6 (b), 7 (c), and 8 (d) in vacuum, N₂ and O₂ atmosphere, $\lambda_{ex} = 340$ nm (100 µs delay) at 298 K.



Figure S76: PL spectra of **5** ($\lambda_{ex} = 260 \text{ nm}$ (a), $\lambda_{ex} = 340 \text{ nm}$ (b)), **6** ($\lambda_{ex} = 260 \text{ nm}$ (a), $\lambda_{ex} = 340 \text{ nm}$ (b)) in ground sample (ground from crystals) at 77 and 298 K.



Figure S77: PL spectra of 7 ($\lambda_{ex} = 260 \text{ nm}$ (a), $\lambda_{ex} = 340 \text{ nm}$ (b)), 8 ($\lambda_{ex} = 260 \text{ nm}$ (a), $\lambda_{ex} = 340 \text{ nm}$ (b)) in ground sample (ground from crystals) at 77 and 298 K.



Figure S78: Phosphorescence spectra of **5** ($\lambda_{ex} = 260 \text{ nm}$ (a), $\lambda_{ex} = 340 \text{ nm}$ (b)), **6** ($\lambda_{ex} = 260 \text{ nm}$ (a), $\lambda_{ex} = 340 \text{ nm}$ (b)) in ground sample (ground from crystals) at 77 and 298 K.



Figure S79: Phosphorescence spectra of 7 ($\lambda_{ex} = 260 \text{ nm}$ (a), $\lambda_{ex} = 340 \text{ nm}$ (b)), 8 ($\lambda_{ex} = 260 \text{ nm}$ (a), $\lambda_{ex} = 340 \text{ nm}$ (b)) in ground sample (ground from crystals) at 77 and 298 K.



Figure S80: Fluorescence spectra of ground sample of **5** at different excitation wavelengths at 298 K.



Figure S81: Fluorescence spectra of ground sample of **6** at different excitation wavelengths at 298 K.



Figure S82: Fluorescence spectra of ground sample of **7** at different excitation wavelengths at 298 K.



Figure S83: Fluorescence spectra of ground sample of **8** at different excitation wavelengths at 298 K.

Table S8. Fluorescence and phosphorescence lifetime of as prepared crystals and groundsamples (ground from crystals) of compounds 5-8

Compounds	Fluorescn	ce lifetime	Phosphorescence lifetime		
_	Ex = 3	330 nm	77	K	298 K
	77 K	298 K	Ex 260 nm	Ex 340 nm	Ex 340 nm
5 Crystals	2.08 ns (41.32%)	1.58 ns (36.94%)	432.77 ms (31.49%)	141.84 ms (58.20%)	80.54 ms (53.23%)
	7.20 ns (58.68%)	6.47 ns (63.06%)	914.84 ms (68.51%)	685.64 ms (41.80%)	263.94 ms (46.77%)
	$(\lambda_{em} = 381 \text{ nm})$	$(\lambda_{em} = 378 \text{ nm})$	$(\lambda_{em} = 410 \text{ nm})$	$(\lambda_{em} = 480 \text{ nm})$	$(\lambda_{em} = 480 \text{ nm})$
5 Ground	1.92 ns (35.79%)	1.72 ns (26.10%)	338.21ms (62.50%)	157.75 ms (75.07%)	n.d.
<u> </u>	8.18 ns (64.21%)	8.21 ns (73.90%)	788.46 (37.50%)	675.91 ms (24.93%)	
	$(\lambda_{em} = 400 \text{ nm})$	$(\lambda_{em} = 375 \text{ nm})$	$(\lambda_{em} = 450 \text{ nm})$	$(\lambda_{em} = 450 \text{ nm})$ $(\lambda_{em} = 475 \text{ nm})$	
6 Crystals	1.72 ns (50.79%)	2.27 ns (57.02%)	217.49 ms (28.55%)	192.96 ms (43.79%)	51.11 ms (31.96%)
0_01ystais	7.52 ns (49.21%)	7.87 ns (42.98%)	1.40 s (71.45%)	1.01 s (56.21%)	315.87 ms (68.04%)
	$(\lambda_{em} = 410 \text{ nm})$	$(\lambda_{em} = 410 \text{ nm})$	$(\lambda_{em} = 425 \text{ nm})$	$(\lambda_{em} = 475 \text{ nm})$	$(\lambda_{em} = 510 \text{ nm})$
6 Ground	3.50 ns (60.79%)	3.23 ns (29.18%)	153.17 ms (65.50%)	149.52 ms (59.30%)	4.42 ms (49.92%)
	12.39 ns (39.21%)	12.79 ns (70.82%)	1.21 s (34.50%)	871.88 ms (40.70%)	23.96 ms (50.08%)
	$(\lambda_{em} = 400 \text{ nm})$	$(\lambda_{em} = 400 \text{ nm})$	$(\lambda_{em} = 450 \text{ nm})$	$(\lambda_{em} = 480 \text{ nm})$	$(\lambda_{em} = 500 \text{ nm})$
7 Crystals	3.60 ns (71.06%)	3.00 ns (75.16%)	52.61 ms (37.61%)	40.24 ms (33.09%)	n.d.
	12.30 ns (28.94%)	10.85 ns (24.84%)	476.41 ms (62.39%)	453.69 ms (66.91%)	
	$(\lambda_{em} = 400 \text{ nm})$	$(\lambda_{em} = 400 \text{ nm})$	$(\lambda_{em} = 455 \text{ nm})$	$(\lambda_{em} = 475 \text{ nm})$	
7 Ground	3.30 ns (67.19%)	2.95 ns (61.22%)	25.27 ms (46.41%)	32.43 ms (54.58%)	n.d.
	12.97 ns (32.81%)	12.92 ns (38.78%)	98.00 ms (32.10%)	295.94 ms (45.42%)	
	$(\lambda_{em} = 460 \text{ nm})$	$(\lambda_{em} = 402 \text{ nm})$	448.33 ms (21.49%)	$(\lambda_{em} = 470 \text{ nm})$	
			$(\lambda_{em} = 470 \text{ nm})$		
8 Crystals	3.61 ns (68.54%)	3.16 ns (70.59%)	46.51 ms (37.57%)	44.98 ms (60.24%)	15.81 ms (60.92%)
	22.54 ns (31.46%)	19.70 ns (29.41%)	374.27 ms (62.43%)	283.37 ms (39.76%)	69.67 ms (39.08%)
	$(\lambda_{em} = 415 \text{ nm})$	$(\lambda_{em} = 416 \text{ nm})$	$(\lambda_{em} = 451 \text{ nm})$	$(\lambda_{em} = 461 \text{ nm})$	$(\lambda_{em} = 529 \text{ nm})$
8 Ground	4.21 ns (69.86%)	3.56 ns (55.78%)	57.97 ms (43.17%)	52.40 ms (44.54%)	n.d.
	21.43 ns (30.14%)	14.25 ns (44.22%)	307.87 ms (56.83%)	281.02 ms (55.46%)	
	$(\lambda_{em} = 420 \text{ nm})$	$(\lambda_{em} = 400 \text{ nm})$	$(\lambda_{em} = 455 \text{ nm})$	$(\lambda_{em} = 460 \text{ nm})$	

* n.d. (not detectable)



Figure S84: PXRD spectra of compound 5 (a), 6 (b), 7 (c), and 8 (d) in crystalline state and ground sample (ground from crystals).



Figure S85: Fluorescence spectra of crystals, ground samples and thin films of compounds 5 (a), 6 (b), 7 (c), and 8 (d) at 298 K, $\lambda_{ex} = 260$ nm. (High energy fluorescence band (intramolecular) intensity decreases in thin films compared to crystals and ground samples).



Figure S86: Fluorescence spectra of thin films of compounds **5** (a), **6** (b), **7** (c), and **8** (d) at 298 K with different excitation wavelength. (Intermolecular fluorescence band at \sim 400 nm is found to be absent in thin films which was present in crystals and ground samples).



Figure S87: Fluorescence spectra of thin films of compounds **5** (a), **6** (b), **7** (c), and **8** (d) at 77 K with different excitation wavelengths.



Figure S88: Phosphorescence spectra of crystals, ground samples and thin films of compounds **5** (a), **6** (b), **7** (c), and **8** (d) at 77 K, $\lambda_{ex} = 260$ nm. (Intramolecular phosphorescence band at ~400 nm is present in thin films like crystals and ground samples).



Figure S89: Phosphorescence spectra of thin films of compounds 5 (a), 6 (b), 7 (c), and 8 (d) at 77 K, $\lambda_{ex} = 260$ nm (100 µs delay).



Figure S90: Excitation spectra of crystals, ground samples and thin films of compounds 5 (a), 6 (b), 7 (c), and 8 (d) at 298 K, $\lambda_{em} = 400$ nm. (Excitation band at ~340 nm corresponding to molecular aggregates is absent in thin films).

6. Theoretical calculations



Figure S91. Frontier molecular orbital energy level diagram of **1-8** obtained from ground state optimized geometry.

Table S9: Summary of TD-DFT computed singlet vertical transitions transitions involved in1-8

Compound	Excited State	E/eV	E/nm	f	Dominant transitions
	(S _n)				(percent contribution)
	1	4.34	285.17	0.1679	HOMO→LUMO
1	2	4.35	284.98	0.1695	HOMO→LUMO+1
	1	4.12	301.26	0.0763	HOMO→LUMO
2	2	4.27	290.57	0.2392	HOMO→LUMO+1
	1	3.85	321.39	0.1814	HOMO→LUMO
3	2	3.86	320.90	0.1831	HOMO→LUMO+1
	1	3.84	322.58	0.2332	HOMO→LUMO
4	2	3.85	321.96	0.2352	HOMO→LUMO+1
	1	5.13	241.56	0.0075	HOMO-1→LUMO
5	2	5.15	240.86	0.0028	HOMO→LUMO+1
	1	4.98	248.79	0.0124	HOMO-1→LUMO
6	2	5.00	247.87	0.0686	HOMO→LUMO
	1	4.81	257.53	0.0081	HOMO-1→LUMO
7	2	4.82	257.46	0.0080	HOMO-2→LUMO
	1	4.79	258.50	0.0050	HOMO-1→LUMO



Figure S92. Frontier molecular orbitals of **1-4** obtained from ground state optimized structure using Gaussian 09 software with B3LYP functional (6-311++G (d, p) for **1**, **2** and 6-311G (d, p) for **3**, **4**).



Figure 93. Frontier molecular orbitals of **5-8** obtained from ground state optimized structure using Gaussian 09 software with B3LYP functional and (6-311++G (d, p) for **6**, **8** and 6-311G (d, p) for **5**, **7**).



Figure S94: Frontier molecular orbitals of **1** in S_0 , S_1 and T_1 state obtained from DFT and TD-DFT calculations using Gaussian 09 software with B3LYP functional and 6-311++G (d,p) basis set in hexane.



Figure S95: Frontier molecular orbitals of **2** in S_0 , S_1 and T_1 state obtained from DFT and TD-DFT calculations using Gaussian 09 software with B3LYP functional and 6-311++G (d,p) basis set in hexane.



Figure S96: Frontier molecular orbitals of **5** in S_0 , S_1 and T_1 state obtained from DFT and TD-DFT calculations using Gaussian 09 software with B3LYP functional and 6-311G (d, p) basis set.



Figure S97: Frontier molecular orbitals of **6** in S_0 , S_1 and T_1 state obtained from DFT and TD-DFT calculations using Gaussian 09 software with B3LYP functional and 6-311++G (d,p) basis set in hexane.



Figure S98. Frontier molecular orbitals of 7 in S_0 , S_1 and T_1 state obtained from DFT and TD-DFT calculations using Gaussian 09 software with B3LYP functional and (6-311G (d,p) for S_0 and T_1 , 6-31G (d,p) for S_1) basis set in hexane.



Figure S99. Frontier molecular orbitals of **8** in S_0 , S_1 and T_1 state obtained from DFT and TD-DFT calculations using Gaussian 09 software with B3LYP functional and (6-311++G (d,p) for S_0 and 6-311G (d,p) for S_1 , T_1) basis set in hexane.



Figure S100: Comparison of important bond parameters (P=O bond length) of crystal structure, ground and excited state optimized geometry (S_0, S_1, T_1) of compound **5**.



Figure S101: Comparison of important bond parameters (P=O bond length) of crystal structure, ground and excited state optimized geometry (S_0, S_1, T_1) of compound 6.



Figure S102: Comparison of important bond parameters (P=O bond length) of crystal structure, ground and excited state optimized geometry (S_0, S_1, T_1) of compound 7.



Figure S103: Comparison of important bond parameters (P=O bond length) of crystal structure, ground and excited state optimized geometry (S_0, S_1, T_1) of compound 8.



Figure S104: Comparison of important bond parameters (P-C bond length) of crystal structure, ground and excited state optimized geometry (S_0, S_1, T_1) of compound 1.



Figure S105: Comparison of important bond parameters (P-C bond length) of crystal structure, ground and excited state optimized geometry (S_0, S_1, T_1) of compound 2.



Figure S106: Comparison of important bond parameters (P-C bond length) of crystal structure, ground and excited state optimized geometry (S_0, T_1) of compound **3**.



Figure S107: Comparison of important bond parameters (P-C bond length) of ground and excited state optimized geometry (S_0, T_1) of compound 4.

Table S10: Summary of theoretical optimized geometrical parameters of **1-4** in S_0 , S_1 and T_1 state

	Bond parameters	1	2	3	4
	P-C (Å)	1.827	1.835	1.834	-
Crystal		1.828	1.835	1.836	
structure		1.829	1.836	1.839	
	Dihedral angle between	83.80	84.71	89.11	-
	two aryl moiety (deg)	78.36	84.06	81.33	
		74.83	75.65	72.10	
	P-C (Å)	1.855	1.855	1.859	1.857
Ground		1.855	1.858	1.859	1.857
state (S_0)		1.855	1.862	1.859	1.858
	Dihedral angle between	89.09°	77.23°	80.58°	80.57°
	two aryl moiety (deg)	89.13°	71.48°	80.36°	80.74°
		89.28°	85.41°	79.57°	81.35°
	P-C (Å)	1.726	1.812	1.771	1.804

Singlet		1.807	1.737	1.820	1.812
state (S ₁)		1.812	1.815	1.836	1.814
	Dihedral angle between	50.15°	74.36°	73.20°	84.55°
	two aryl moiety (deg)	75.25°	66.10°	77.65°	85.16°
		86.89°	82.55°	84.73°	82.61°
	P-C (Å)	1.737	1.819	1.843	1.834
Triplet		1.807	1.854	1.999	1.994
state (T_1)		1.835	1.754	1.999	1.995
	Dihedral angle between	69.85°	89.78°	86.27°	86.11°
	two aryl moiety (deg)	69.94°	81.95°	87.69°	89.05°
		68.60°	77.11°	86.13°	87.39°

	Bond parameters	5	6	7	8
	P-C (Å)	1.799	1.811	1.828	1.827, 1.831, 1.848
Crystal		1.803	1.812	1.834	1.830, 1.832, 1.838
structure		1.807	1.820	1.835	
	P=O (Å)	1.486	1.477	1.489	1.487, 1.491
	Dihedral angle	82.43	89.39	85.05	72.91, 76.23, 82.43
	between two aryl	80.22	78.86	77.91	72.20, 74.33, 85.68
	moiety (deg)	76.94	75.85	71.95	
	P-C (Å)	1.834	1.866	1.866	1.862
Ground		1.834	1.866	1.866	1.863
state (S_0)		1.835	1.866	1.866	1.863
	P=O (Å)	1.500	1.509	1.510	1.510
	Dihedral angle	73.95°	78.02°	78.87°	78.00°
	between two aryl	69.62°	79.87°	78.98°	78.09°
	moiety (deg)	71.55°	79.80°	79.26°	78.62°
	N-C (Å)	1.711	1.733	1.826	1.770
Singlet		1.811	1.843	1.842	1.835
state (S_1)		1.859	1.833	1.933	1.916
	P=O (Å)	1.587	1.593	1.616	1.592
	Dihedral angle	77.55°	81.84°	86.14	76.22°
	between two aryl	63.35°	70.45°	72.61	67.93°
	moiety (deg)	53.34°	79.36°	70.90	77.82°
	N-C (Å)	1.829	1.839	1.854	1.850
Triplet		1.831	1.841	1.867	1.864
state (T_1)		1.832	1.843	1.869	1.865
	P=O (Å)	1.502	1.510	1.510	1.508
	Dihedral angle	62.25°	78.67°	83.81°	82.94°
	between two aryl	82.04°	55.19°	41.37°	81.97°
	moiety (deg)	63.40°	81.87°	81.92°	42.12°

Table S11: Summary of theoretical optimized geometrical parameters of **5-8** in S_0 , S_1 and T_1 state



Figure S108. Energy level diagram showing singlet-triplet energy gap and possible ISC channel of **1**, and **2** (energy levels in diagram are not up-to scale) (calculated from singlet and triplet vertical transitions). (Green color arrow: Other possible ISC channels from $S_1 \rightarrow T_n$).



Figure S109. Energy level diagram showing singlet-triplet energy gap and possible ISC channel of **3**, and **4** (energy levels in diagram are not up-to scale) (calculated from singlet and triplet vertical transitions). (Green color arrow: Other possible ISC channels from $S_1 \rightarrow T_n$).



Figure S110. Energy level diagram showing singlet-triplet energy gap and possible ISC channel of **5**, and **6** (energy levels in diagram are not up-to scale) (calculated from singlet and triplet vertical transitions). (Green color arrow: Other possible ISC channels from $S_1 \rightarrow T_n$).



Figure S111. Energy level diagram showing singlet-triplet energy gap and possible ISC channel of 7, and 8 (energy levels in diagram are not up-to scale) (calculated from singlet and triplet vertical transitions). (Green color arrow: Other possible ISC channels from $S_1 \rightarrow T_n$).

Compound	$ES_0 (eV) (DM^*)$	$\mathrm{ES}_{1}\left(\mathrm{eV}\right)\left(\mathrm{DM}^{*}\right)$	$ET_1 (eV) (DM^*)$
1	-28204.62 (1.54 D)	-28201.24 (2.49 D)	-28201.36 (4.42 D)
2	-31414.81 (1.06 D)	-31413.96 (1.96 D)	-31411.70 (3.10 D)
3	-34624.25 (0.60 D)	-34614.35 (1.57 D)	-34614.82 (1.05 D)
4	-37834.80 (0.78 D)	-37824.09 (1.82 D)	-37824.52 (1.31 D)
5	-30252.64 (4.33 D)	-30248.57 (5.48 D)	-30249.03 (4.51 D)
6	-33463.22 (4.28 D)	-33458.96 (5.81 D)	-33459.74 (4.20 D)
7	-36672.69 (3.80 D)	-36662.24 (4.56 D)	-36669.52 (3.95 D)
8	-39883.22 (4.11 D)	-39879.00 (6.03 D)	-39879.71 (3.24 D)

Table S12: Energy level of S_0 , S_1 and T_1 (eV) calculated from ground and excited state geometry optimization.

*DM = Dipole moment in Debye

Table S13: Energy difference between singlet and triplet state (ΔE_{S1T1}) (eV)

Compound	Theoretical	Theoretical	Experimental	Experimental
	(ΔE_{S1T1}) (eV)	(ΔE_{S1T1}) (eV)	(ΔE_{S1T1}) (eV)	(ΔE_{S1T1}) (eV)
	(From vertical	(From optimized	(Intramolecular)	(Inter molecular)
	transitions)	geometry)		
1	0.79	0.12	0.02*	0.54
2	0.66	2.26	0.10	nd
3	0.61	0.47	0.31	nd
4	0.53	0.43	0.36	nd
5	1.43	0.46	1.08	0.71
6	1.34	0.78	1.06	0.55
7	1.27	7.28	0.78	0.63
8	1.30	0.71	0.86	0.68

* Difficult to measure precisely as wavelength difference between fluorescence and phosphorescence spectra is very less^{XX} nd: non-detectable

7. References

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