Luminescent materials containing multiple benzoxaphosphole units

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1. General considerations

All operations were performed under nitrogen atmosphere, using Schlenk line or within a Vacuum Atmospheres MBraun glove box unless otherwise stated. Tetrahydrofuran, hexanes, and toluene were dried by distillation from sodium benzophenone ketyl. Triethylamine was purified by distillation and degassed with nitrogen prior to use. Hexanes was dried by passing through neutral alumina column and degassed with nitrogen prior to use for UV-vis and fluorescence measurements. Dichloromethane was dried by distillation from CaH_2 prior to use for UV-vis and fluorescence measurements. Terephthaloyl chloride, naphthalene-2,6-dicarbonyl dichloride, thiophene-2,5-dicarbonyl dichloride and 1,3,5-benzenetricarbonyl trichloride were prepared according to the literature.[1] 3,5-di-*tert*-butyl-2-phosphinophenol was synthesized by published procedure.[2] ^{1}H, ^{13}C{^{1}H} and ^{31}P{^{1}H} NMR spectra were recorded on a Varian INOVA AS-400 or 600 spectrometers, and all chemical shifts are referred to residual $CHCl_3$ signals (for ^{1}H and ^{13}C{^{1}H} NMR spectra) or to an external sample of 85% H_3PO_4 (for ^{31}P{^{1}H} NMR spectra). Melting points were measured on a Mel-temp melting point apparatus. High resolution mass spectrometry was performed by the University of Michigan Mass Spectrometry facility using a VG (Micromass) 70-250-S magnetic sector spectrometer. UV-Vis and fluorescence data were recorded using a Cary 50 Bio UV-Visible spectrophotometer and a Cary Eclipse spectrometer, respectively. Excitation wavelengths were chosen for fluorescence measurements to be at the adsorption maxima for each compound. Anthracene in ethanol was used as the quantum yield standard for **4**, 9,10-diphenylanthracene in cyclohexane was used as the quantum yield standard for **1** and **2**, and fluorescein in 0.1 M NaOH was used as the quantum yield standard for **3**.[3]

2. Experimental

1,4-Bis(4',6'-di-*tert*-butylbenzoxaphospholyl)benzene (1)

To a solution of 3,5-di-*tert*-butyl-2-phosphinophenol (1.3 g, 5.5 mmol) in 10 mL THF was added triethylamine (0.77 mL, 5.5 mmol), followed by a solution of terephthaloyl chloride (0.57 g, 2.8 mmol) in 10 mL THF. The mixture was stirred at room temperature overnight to give a yellow cloudy solution. A white precipitate was removed by filtration and the solvent was removed under vacuum to yield a yellow solid. The solid was dissolved in 10 mL toluene, and the solution was refluxed for 72 hours to yield a yellow cloudy solution. After the reaction was cooled to room temperature, the solvent was removed under vacuum to give a yellow solid. The solid was extracted with hexanes and then the solution was passed through basic alumina twice to give a yellow solution. The solvent was removed *in vacuo* to yield a yellow solid. Yield: 0.43 g (27%). mp: 225-227 °C. ^1H NMR (400 MHz, CDCl$_3$): δ 8.07 (s, 4H, Ar), 7.65 (s, 2H, Ar), 7.33 (s, 2H, Ar), 1.61 (s, 18H, *t*-Bu), 1.42 (s, 18H, *t*-Bu). $^{31}P\{^1H\}$ NMR (161 MHz, CDCl$_3$): δ 93.3 (s, 1P). $^{13}C\{^1H\}$ NMR (150 MHz, CDCl$_3$): δ 192.4 (d, J_{pc} = 55.5 Hz), 161.5, 151.4, 135.4, 135.3, 130.8 (d, J_{pc}= 46.5 Hz), 125.0, 117.4, 108.1, 37.0, 35.3, 31.5, 31.1. UV (CH$_2$Cl$_2$): λ_{max}/nm 418, 437sh (ε/M^{-1}·cm^{-1} 11305, 9205). Fluorescence (CH$_2$Cl$_2$): λ_{em}/nm 462, 485sh. Quantum Yield (CH$_2$Cl$_2$): Φ 0.31. HRMS (EI, 70 ev): m/z 570.2813 (Calc. 570.2817).

2,6-Bis(4',6'-di-*tert*-butylbenzoxaphospholyl)naphthalene(2)

To a solution of 3,5-di-*tert*-butyl-2-phosphinophenol (1.4 g, 5.9 mmol) in 10 mL THF was added triethylamine (0.83 mL, 5.9 mmol), followed by a solution of naphthalene-2,6-dicarbonyl dichloride (0.75 g, 3.0 mmol) in 10 mL THF. The mixture was stirred at room temperature overnight to produce a yellow cloudy solution. A white precipitate was removed by filtration and the solvent was removed under vacuum to yield a yellow solid. The solid was dissolved in 10 mL toluene, and the solution was refluxed

for 72 hours to give a yellow cloudy solution. After the reaction was cooled to room temperature, the solvent was removed *in vacuo* to give a yellow solid. The solid was extracted with hexanes and then the solution was passed through basic alumina to give a yellow solution. The solvent was removed under vacuum to give a yellow solid. Yield: 0.37 g (20%). mp: 309-312 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.46 (s, 2H, Ar), 8.15 (m, 2H, Ar), 7.93 (m, 2H, Ar), 7.69 (s, 2H, Ar), 7.34 (s, 2H, Ar), 1.63 (s, 18H, *t*-Bu), 1.43 (s, 18H, *t*-Bu). ^{31}P{^{1}H} NMR (161 MHz, CDCl$_3$): δ 95.0 (s, 1P). ^{13}C{^{1}H} NMR (150 MHz, CDCl$_3$): δ 192.8 (d, J_{pc} = 55.5 Hz), 161.6, 151.5, 151.4, 133.9, 132.8, 132.7, 130.7 (d, J_{pc} = 43.5 Hz), 129.2, 124.2, 122.5, 117.4, 108.1, 37.0, 35.3, 31.5, 31.1. UV (CH$_2$Cl$_2$): λ_{max}/nm 412, 438sh (ε/M^{-1}·cm^{-1} 11570, 10194). Fluorescence (CH$_2$Cl$_2$): λ_{em}/nm 462sh, 473. Quantum Yield (CH$_2$Cl$_2$): Φ 0.50. HRMS (EI, 70 ev): m/z 620.2959 (Calc. 620.2973).

2,5-Bis(4',6'-di-*tert*-butylbenzoxaphospholyl)thiophene (3)

To a solution of 3,5-di-*tert*-butyl-2-phosphinophenol (1.0 g, 4.2 mmol) in 10 mL THF was added triethylamine (0.59 mL, 4.2 mmol), followed by a solution of thiophene-2,5-dicarbonyl dichloride (0.44 g, 2.1 mmol) in 10 mL THF. The mixture was stirred at room temperature overnight to produce a brown cloudy solution. A white precipitate was removed by filtration and the solvent was removed under vacuum to yield a red solid. The solid was dissolved in 10 mL toluene, and the solution was refluxed overnight to give a red solution. After the reaction was cooled to room temperature, the solvent was removed under vacuum to give a red solid. The solid was extracted with hexanes and then the solution was passed through basic alumina three times to give a red solution. The solvent was removed *in vacuo* to yield a red solid. Yield: 0.19 g (16%). mp: 178-182 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.62 (s, 2H, Ar), 7.58 (s, 2H, Ar), 7.31 (s, 2H, Ar), 1.59 (t, 18H, *t*-Bu), 1.41 (s, 18H, *t*-Bu). ^{31}P{^{1}H} NMR (161 MHz, CDCl$_3$): δ 91.2 (s, 1P). ^{13}C{^{1}H} NMR (150 MHz, CDCl$_3$): δ 185.8 (d, J_{pc} = 52.5 Hz), 160.8, 151.5, 151.4, 138.7, 130.9 (d, J_{pc} = 48 Hz), 125.9, 117.6, 108.0, 37.0, 35.3, 31.5, 31.1. UV (CH$_2$Cl$_2$): λ_{max}/nm 457 (ε/M^{-1}·cm^{-1} 32283). Fluorescence (CH$_2$Cl$_2$): λ_{em}/nm 533. Quantum Yield (CH$_2$Cl$_2$): Φ 0.12. HRMS (EI, 70

ev): m/z 576.2401 (Calc. 576.2381).

1,3,5-Tris(4',6'-di-*tert*-butyl-benzoxaphospholyl)benzene (4)

To a solution of 3,5-di-*tert*-butyl-2-phosphinophenol (1.0 g, 4.2 mmol) in 10 mL THF was added triethylamine (0.59 mL, 4.2 mmol), followed by a solution of 1,3,5-benzenetricarbonyl trichloride (0.37 g, 1.4 mmol) in 10 mL THF. The mixture was stirred at room temperature overnight to produce a yellow cloudy solution. A white precipitate was removed by filtration and the solvent was removed under vacuum to yield a yellow solid. The solid was dissolved in 10 mL toluene, and the reaction was refluxed for 96 hours to produce a yellow cloudy solution. After the reaction was cooled to room temperature, the solvent was removed under vacuum to give a yellow solid. The solid was extracted with hexanes twice, and the combined filtrates were evaporated under vacuum to yield a yellow solid. The crude product was purified by flash column chromatography using hexanes as the eluant. The solvent was removed under vacuum to give a yellow solid. Yield: 0.21 g (18%). mp: > 320 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.65 (s, 3H, Ar), 7.78 (s, 3H, Ar), 7.37 (s, 3H, Ar), 1.65 (s, 27H, *t*-Bu), 1.45 (s, 27H, *t*-Bu). ^{31}P{^{1}H} NMR (161 MHz, CDCl$_3$): δ 94.9 (s, 1P). ^{13}C{^{1}H} NMR (150 MHz, CDCl$_3$): δ 192.0 (d, J_{pc} =54.0 Hz), 161.6 (d, J_{pc} = 15.0 Hz), 151.5, 151.4, 135.9, 130.6 (d, J_{pc} = 45.0 Hz), 121.0, 117.5, 108.4, 37.0, 35.3, 31.5, 31.2. UV (CH$_2$Cl$_2$): λ$_{max}$/nm 362 (ε/M^{-1}·cm^{-1} 28214). Fluorescence (CH$_2$Cl$_2$): λ$_{em}$/nm 437, 451sh. Quantum Yield (CH$_2$Cl$_2$): Φ 0.14. HRMS (EI, 70 ev): m/z 816.4010 (Calc. 816.3990).

3. X-ray crystallographic data

Single crystal X-ray details for compound **1** are accessible in the accompanying cif file (CCDC 1007938). For further details see Table S1-S5.   A severely disordered solvent molecule (hexane) was located in the asymmetric unit, but modeling it proved impossible. The solvent contributions were treated using SQUEEZE which found 37 electrons corresponding to approximately one molecule of hexane; it is included in the formula and the computation of the intensive properties.

Table S1 Crystal data and structure refinement for **1**.

Empirical formula	$C_{42}H_{58}O_2P_2$
Formula weight	656.82
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	a = 6.5471(4) Å a = 100.773(2)°
	b = 10.5862(6) Å β =101.934 (2)°
	c = 14.3323(9) Å γ =107.345(2)°
Volume	895.07 (9) Å ^{3}
Z	1
Calculated density	1.219 Mg/m^3
Absorption coefficient	0.157 mm^{-1}
F(000)	356
Crystal size	0.24×0.20×0.11 mm
θ range for data collection	1.51 to 26.49°
Limiting indices	-8≤h≤8, -11≤k≤13,
	-17≤l≤17
Reflections collected	11737
Completeness to θ =26.49º	98.7 %
Absorption correction	Multi-Scan
Max. and min. transmission	0.9829 and 0.9633
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3677/0/187
Goodness-of-fit on F^2	1.002
Final R indices [I>2σ(I)]	R1=0.0352, wR2=0.1204
R indices (all data)	R1=0.0419, wR2=0.1273
Largest diff. peak and hole	0.347 and -0.175 e.A^{-3}

Table S2 Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters ($Å^2×10^3$) for **1**.

	x	y	z	U(eq)
P(1)	6622(1)	1916(1)	1593(1)	14(1)
O(1)	6088(2)	-663(1)	1499(1)	14(1)
C(1)	1405(2)	-3278(1)	3398(1)	22(1)
C(2)	1126(2)	-1875(1)	3620(1)	15(1)
C(3)	2477(2)	-889(1)	3122(1)	14(1)
C(4)	3685(2)	-1288(1)	2513(1)	14(1)
C(5)	4859(2)	-314(1)	2109(1)	13(1)
C(6)	7105(2)	438(1)	1179(1)	14(1)
C(7)	8548(2)	194(1)	564(1)	14(1)
C(8)	9326(2)	-900(1)	561(1)	16(1)
C(9)	9237(2)	1083(1)	-3(1)	16(1)
C(10)	1919(2)	-1260(2)	4745(1)	20(1)
C(11)	2513(2)	478(1)	3299(1)	14(1)
C(12)	3716(2)	1459(1)	2916(1)	12(1)
C(13)	4921(2)	1035(1)	2271(1)	13(1)
C(14)	3873(2)	2963(1)	3214(1)	14(1)
C(15)	3138(2)	3459(1)	2300(1)	18(1)
C(16)	2404(2)	3179(2)	3892(1)	20(1)
C(17)	6311(2)	3856(1)	3780(1)	20(1)
C(18)	-1358(2)	-2081(2)	3242(1)	21(1)

U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Table S3 Bond lengths [Å] and angles [°] for **1**.

P(1)-C(6)	1.7117(14)	C(9)-H(5)	0.9300
P(1)-C(13)	1.7951(13)	C(10)-H(2)	0.9600
O(1)-C(6)	1.3701(16)	C(10)-H(17)	0.9600
O(1)-C(5)	1.3769(15)	C(10)-H(18)	0.9600
C(1)-C(2)	1.5334(19)	C(11)-C(12)	1.3812(18)
C(1)-H(15)	0.9600	C(11)-H(22)	0.9300
C(1)-H(1)	0.9600	C(12)-C(13)	1.4268(17)
C(1)-H(16)	0.9600	C(12)-C(14)	1.5366(18)
C(2)-C(10)	1.5344(19)	C(14)-C(16)	1.5358(18)
C(2)-C(18)	1.5381(18)	C(14)-C(15)	1.5387(19)
C(2)-C(3)	1.5404(17)	C(14)-C(17)	1.5424(19)
C(3)-C(4)	1.3825(17)	C(15)-H(8)	0.9600
C(3)-C(11)	1.4157(18)	C(15)-H(7)	0.9600
C(4)-C(5)	1.3880(18)	C(15)-H(6)	0.9600
C(4)-H(3)	0.9300	C(16)-H(9)	0.9600
C(5)-C(13)	1.3917(19)	C(16)-H(10)	0.9600
C(6)-C(7)	1.4625(17)	C(16)-H(11)	0.9600
C(7)-C(9)	1.3917(19)	C(17)-H(14)	0.9600
C(7)-C(8)	1.3978(19)	C(17)-H(12)	0.9600
C(8)-C(9)#1	1.3868(18)	C(17)-H(13)	0.9600
C(8)-H(4)	0.9300	C(18)-H(20)	0.9600
C(9)-C(8)#1	1.3868(18)	C(18)-H(21)	0.9600
C(18)-H(19)	0.9600	C(5)-C(4)-H(3)	121.2
C(1)-C(2)-C(10)	108.16(11)	O(1)-C(5)-C(4)	119.63(12)
C(1)-C(2)-C(18)	108.77(11)	O(1)-C(5)-C(13)	115.32(11)
C(10)-C(2)-C(18)	109.25(11)	C(4)-C(5)-C(13)	125.05(12)
C(1)-C(2)-C(3)	111.86(11)	O(1)-C(6)-C(7)	114.63(11)
C(10)-C(2)-C(3)	109.53(10)	O(1)-C(6)-P(1)	116.22(9)
C(18)-C(2)-C(3)	109.23(10)	C(7)-C(6)-P(1)	129.08(10)
C(4)-C(3)-C(11)	118.52(12)	C(9)-C(7)-C(8)	118.68(12)
C(4)-C(3)-C(2)	122.25(12)	C(9)-C(7)-C(6)	120.27(12)
C(11)-C(3)-C(2)	119.22(11)	C(8)-C(7)-C(6)	121.01(12)
C(3)-C(4)-C(5)	117.54(12)	C(9)#1-C(8)-C(7)	120.16(12)
C(3)-C(4)-H(3)	121.2	C(6)-P(1)-C(13)	88.50(6)
C(9)#1-C(8)-H(4)	119.9	C(12)-C(11)-H(22)	117.9

C(7)-C(8)-H(4)	119.9	C(3)-C(11)-H(22)	117.9
C(8)#1-C(9)-C(7)	121.16(13)	C(11)-C(12)-C(13)	117.05(12)
C(8)#1-C(9)-H(5)	119.4	C(11)-C(12)-C(14)	121.85(11)
C(7)-C(9)-H(5)	119.4	C(13)-C(12)-C(14)	121.00(11)
C(2)-C(10)-H(2)	109.5	C(5)-C(13)-C(12)	117.60(12)
C(2)-C(10)-H(17)	109.5	C(5)-C(13)-P(1)	109.66(9)
H(2)-C(10)-H(17)	109.5	C(12)-C(13)-P(1)	132.73(10)
C(2)-C(10)-H(18)	109.5	C(16)-C(14)-C(12)	112.09(11)
H(2)-C(10)-H(18)	109.5	C(16)-C(14)-C(15)	107.46(11)
H(17)-C(10)-H(18)	109.5	C(12)-C(14)-C(15)	111.32(11)
C(12)-C(11)-C(3)	124.19(12)	C(16)-C(14)-C(17)	108.01(11)
C(12)-C(14)-C(17)	108.60(10)	C(14)-C(16)-H(11)	109.5
C(15)-C(14)-C(17)	109.27(11)	H(9)-C(16)-H(11)	109.5
C(14)-C(15)-H(8)	109.5	H(10)-C(16)-H(11)	109.5
C(14)-C(15)-H(7)	109.5	C(14)-C(17)-H(14)	109.5
H(8)-C(15)-H(7)	109.5	C(14)-C(17)-H(12)	109.5
C(14)-C(15)-H(6)	109.5	H(14)-C(17)-H(12)	109.5
H(8)-C(15)-H(6)	109.5	C(14)-C(17)-H(13)	109.5
H(7)-C(15)-H(6)	109.5	H(14)-C(17)-H(13)	109.5
C(14)-C(16)-H(9)	109.5	H(12)-C(17)-H(13)	109.5
C(14)-C(16)-H(10)	109.5	C(2)-C(18)-H(20)	109.5
C(2)-C(18)-H(21)	109.5	C(2)-C(18)-H(19)	109.5
H(20)-C(18)-H(21)	109.5	H(20)-C(18)-H(19)	109.5
H(21)-C(18)-H(19)	109.5	C(2)-C(18)-H(21)	109.5
C(6)-O(1)-C(5)	110.30(10)	H(9)-C(16)-H(10)	109.5
C(2)-C(1)-H(15)	109.5	C(2)-C(1)-H(1)	109.5
C(2)-C(1)-H(1)	109.5	H(15)-C(1)-H(16)	109.5
H(15)-C(1)-H(1)	109.5	H(1)-C(1)-H(16)	109.5

Symmetry transformations used to generate equivalent atoms: #1 -x+2,-y,-z

Table S4 Anisotropic displacement parameters ($\text{Å}^2 \times 10^3$) for **1**.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
P(1)	17(1)	13(1)	17(1)	6(1)	11(1)	6(1)
O(1)	16(1)	13(1)	18(1)	5(1)	12(1)	6(1)
C(1)	26(1)	16(1)	30(1)	12(1)	16(1)	8(1)
C(2)	15(1)	16(1)	19(1)	8(1)	10(1)	6(1)
C(3)	12(1)	15(1)	14(1)	5(1)	4(1)	4(1)
C(4)	15(1)	11(1)	16(1)	4(1)	7(1)	5(1)
C(5)	12(1)	16(1)	12(1)	3(1)	6(1)	6(1)
C(6)	13(1)	16(1)	13(1)	6(1)	6(1)	4(1)
C(7)	12(1)	16(1)	12(1)	1(1)	5(1)	4(1)
C(8)	19(1)	17(1)	15(1)	8(1)	10(1)	7(1)
C(9)	19(1)	18(1)	17(1)	7(1)	9(1)	10(1)
C(10)	23(1)	21(1)	19(1)	10(1)	11(1)	7(1)
C(11)	14(1)	17(1)	13(1)	3(1)	7(1)	7(1)
C(12)	13(1)	14(1)	12(1)	3(1)	4(1)	5(1)
C(13)	12(1)	15(1)	13(1)	4(1)	5(1)	4(1)
C(14)	19(1)	12(1)	16(1)	4(1)	9(1)	6(1)
C(15)	22(1)	17(1)	21(1)	7(1)	10(1)	10(1)
C(16)	30(1)	15(1)	22(1)	6(1)	16(1)	11(1)
C(17)	23(1)	14(1)	22(1)	2(1)	6(1)	5(1)
C(18)	16(1)	24(1)	27(1)	13(1)	9(1)	5(1)

The anisotropic displacement factor exponent takes the form: $-2\pi^2[\, h^2\, a^{*2}U^{11} + ... + 2\, h\, k\, a^*\, b^*\, U^{12}]$

Table S5 Hydrogen coordinates (×10^4) and isotropic displacement parameters (Å^2 ×10 ^{3}) for **1**.

	x	y	z	U(eq)
H(15)	2955	-3158	3614	32
H(1)	843	-3702	2699	32
H(16)	590	-3850	3741	32
H(3)	3710	-2175	2380	16
H(4)	8878	-1506	934	19
H(5)	8725	1812	-9	19
H(2)	1782	-373	4899	30
H(17)	3450	-1171	4987	30
H(18)	1021	-1851	5052	30
H(22)	1672	732	3699	17
H(8)	3304	4408	2507	27
H(7)	1605	2926	1959	27
H(6)	4047	3353	1866	27
H(9)	2531	4126	4052	30
H(10)	2882	2931	4489	30
H(11)	879	2616	3559	30
H(14)	6433	4800	3970	31
H(12)	7257	3758	3362	31
H(13)	6760	3567	4361	31
H(20)	-1554	-1210	3383	32
H(21)	-2201	-2673	3566	32
H(19)	-1871	-2490	2540	32

4. NMR spectra

^{31}P{^{1}H} NMR spectrum of 1,4-bis(4',6'-di-*tert*-butylbenzoxaphospholyl)benzene (**1**)
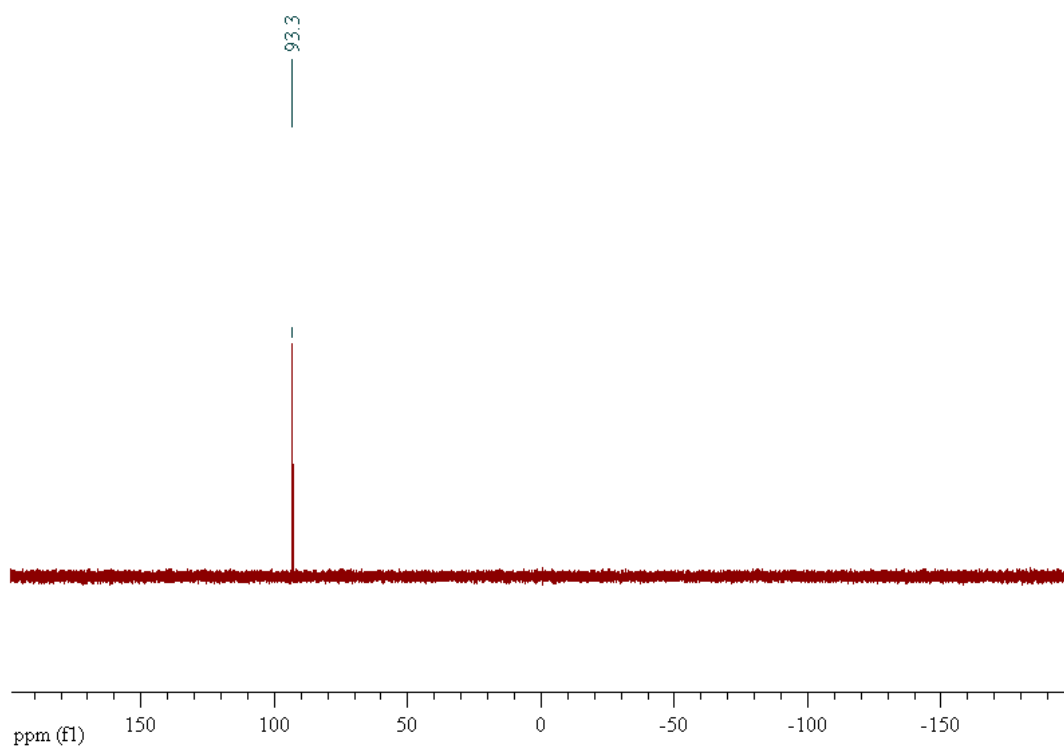
^{1}H NMR spectrum of 1,4-bis(4',6'-di-*tert*-butylbenzoxaphospholyl)benzene (**1**)
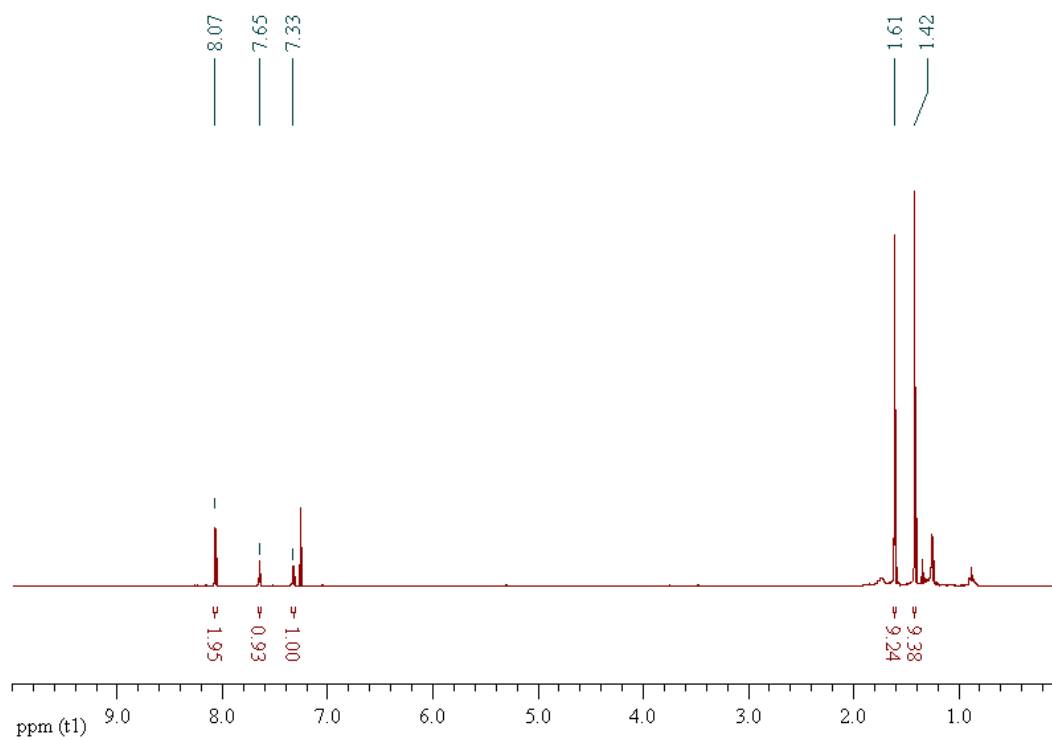
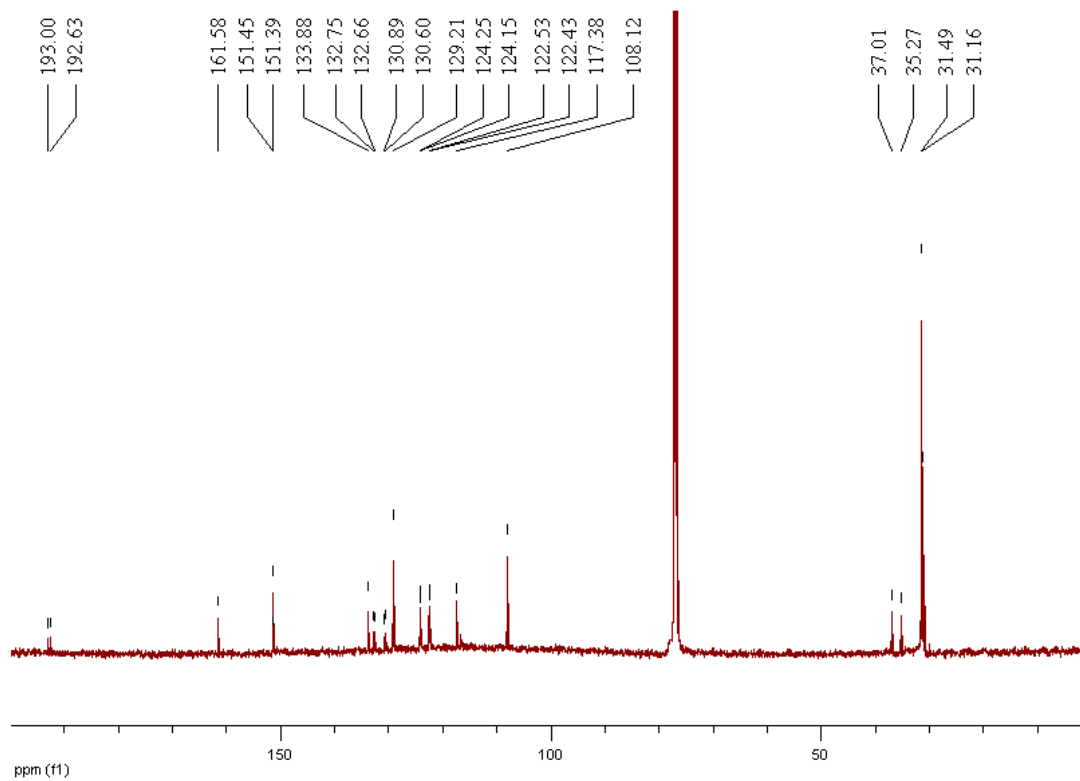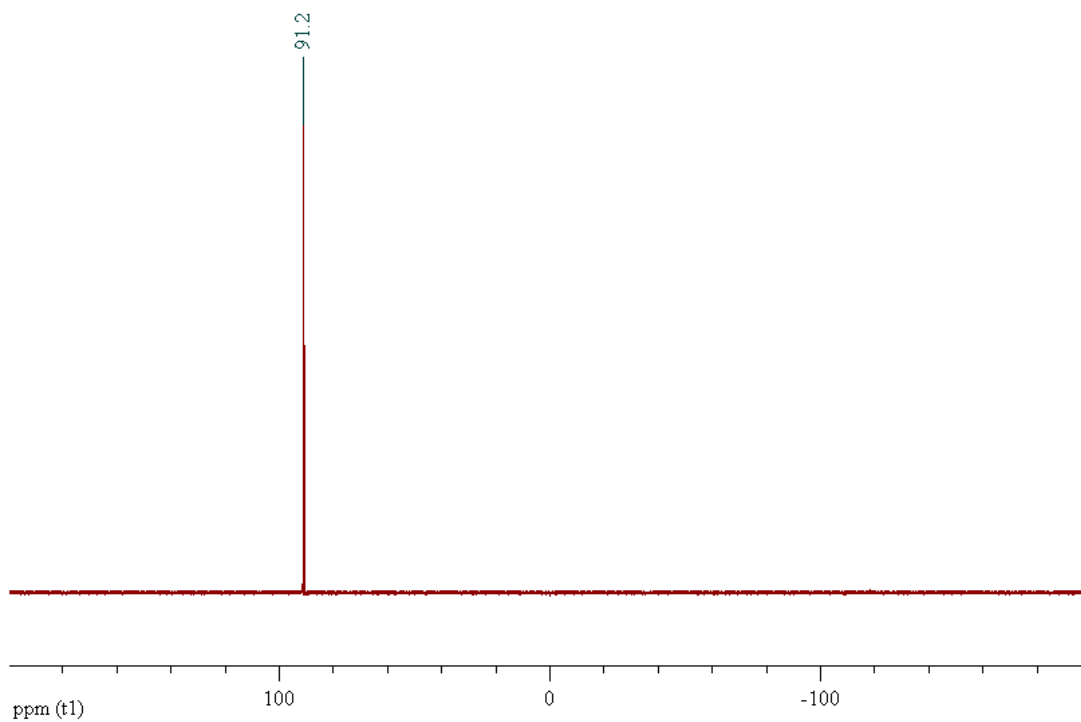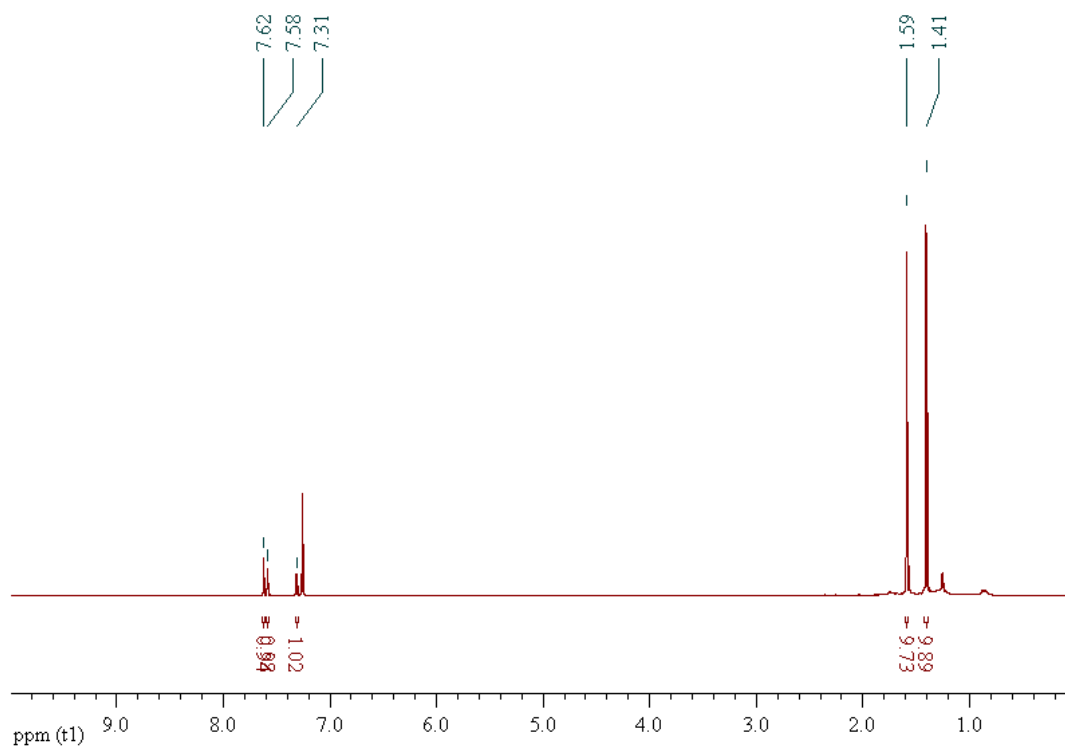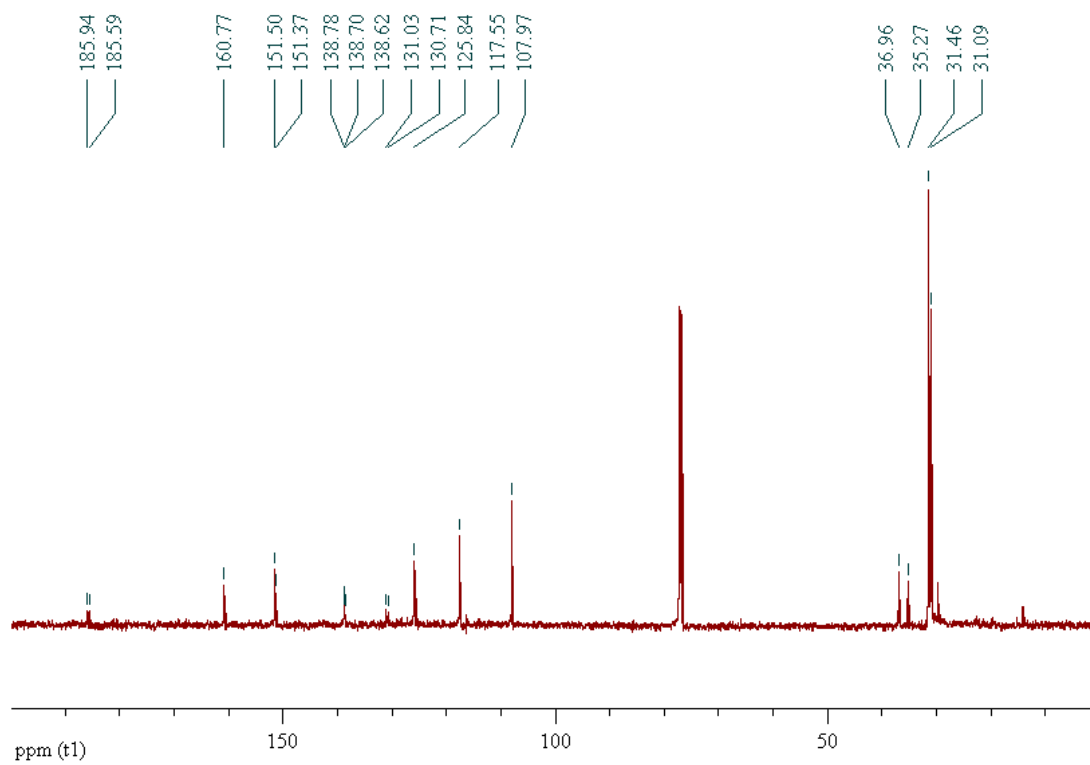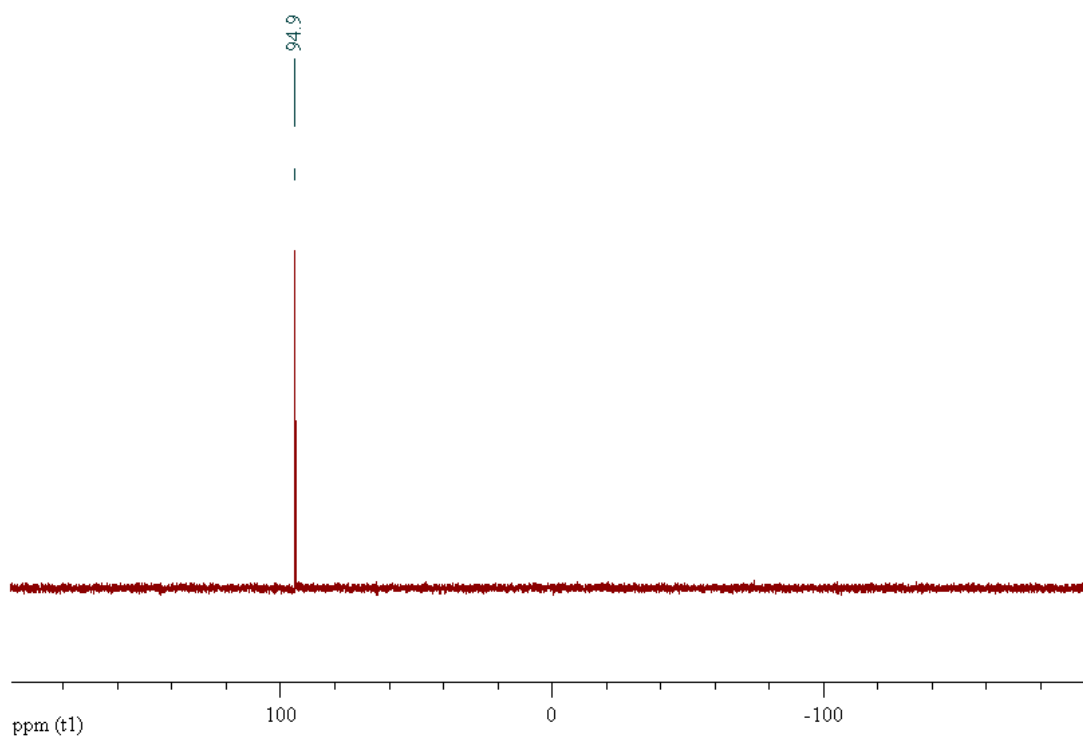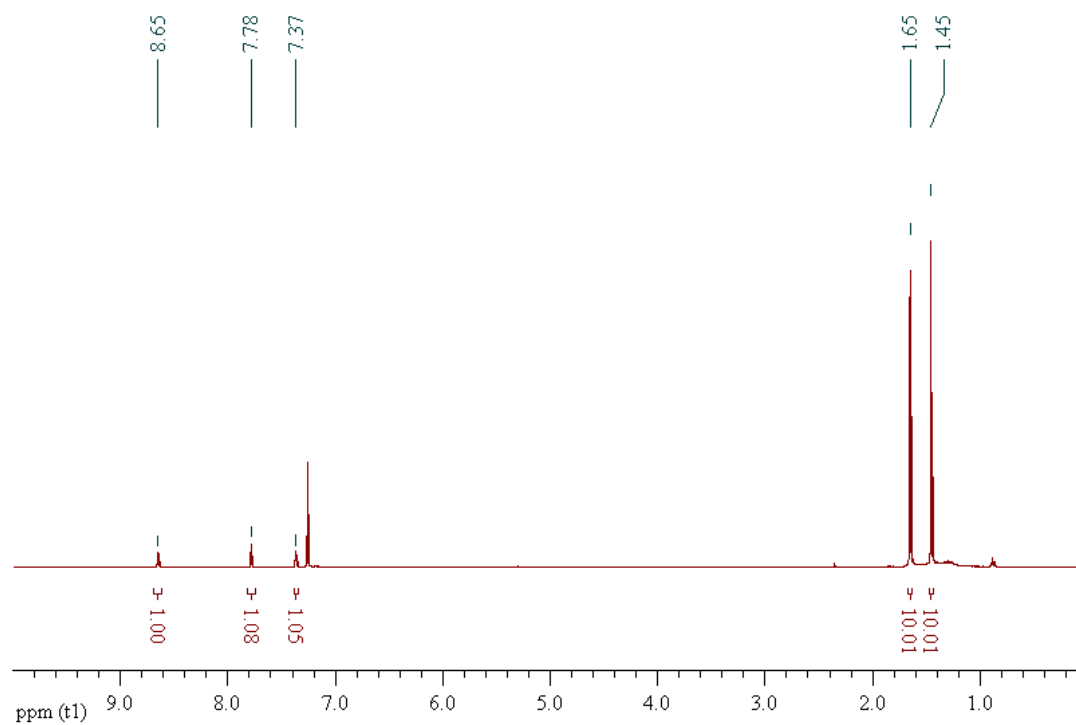## $^{13}C\{^1H\}$ NMR spectrum of 1,4-bis(4',6'-di-*tert*-butylbenzoxaphospholyl)benzene (**1**)
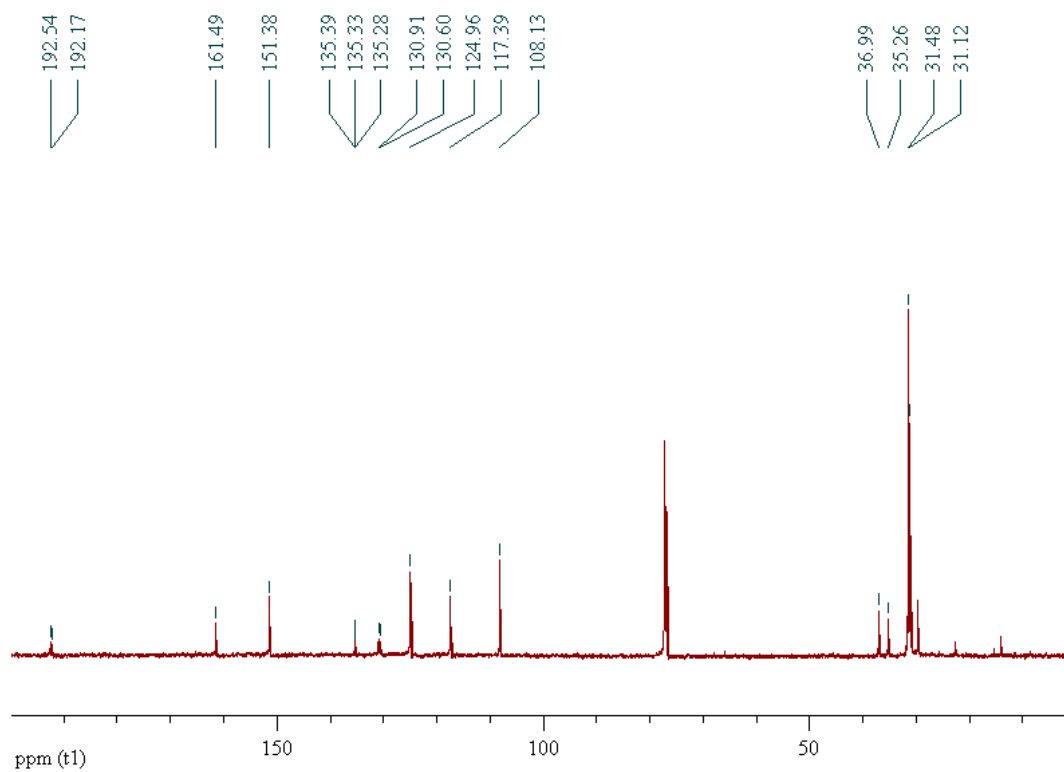
192.54
192.17
161.49
151.38
135.39
135.33
135.28
130.91
130.60
124.96
117.39
108.13
36.99
35.26
31.48
31.12

ppm (t1)   150   100   50

$^{31}P\{^1H\}$ NMR spectrum of 2,6-bis(4',6'-di-*tert*-butylbenzoxaphospholyl)naphthalene(**2**)

95.0

ppm (f1)   150   100   50   0   -50   -100   -150

¹H NMR spectrum of 2,6-bis(4',6'-di-*tert*-butylbenzoxaphospholyl)naphthalene(**2**)

8.46 8.16 8.14 7.94 7.92 7.69 7.34   1.63 1.43

1.00 1.01 1.00 1.01 1.09   9.54 9.80

ppm (t1) 9.0   8.0   7.0   6.0   5.0   4.0   3.0   2.0   1.0

¹³C{¹H} NMR spectrum of 2,6-bis(4',6'-di-*tert*-butylbenzoxaphospholyl)naphthalene(**2**)

193.00 192.63   161.58 151.45 151.39 133.88 132.75 132.66 130.89 130.60 129.21 124.25 124.15 122.53 122.43 117.38 108.12   37.01 35.27 31.49 31.16

ppm (f1)   150   100   50
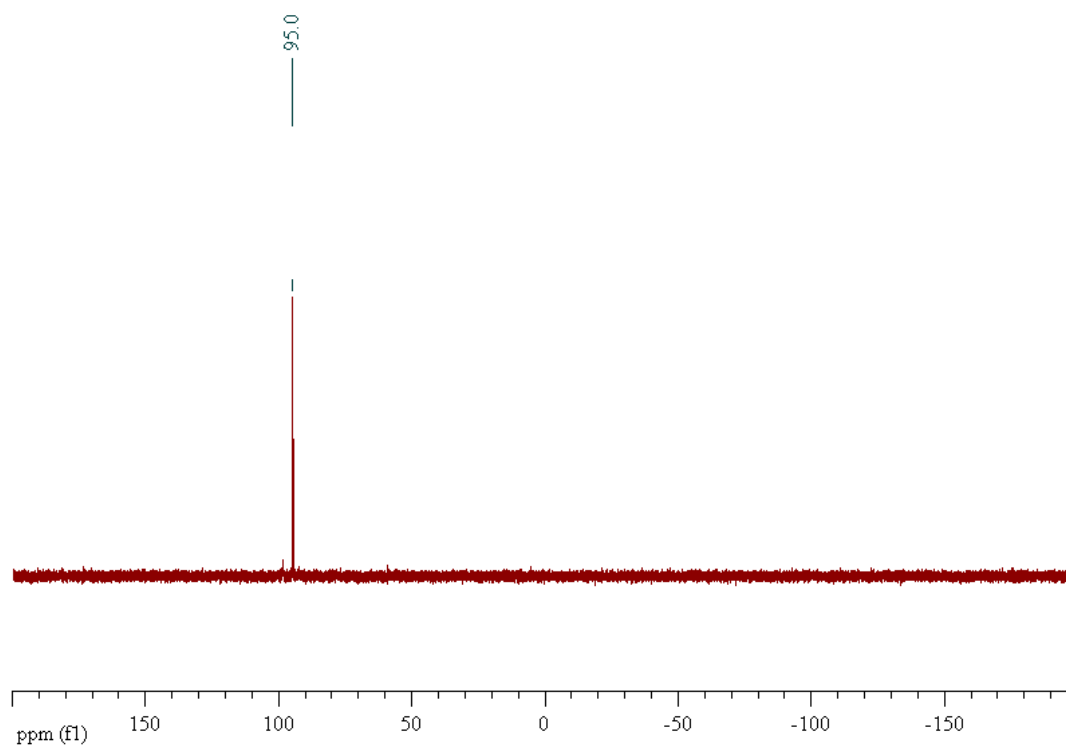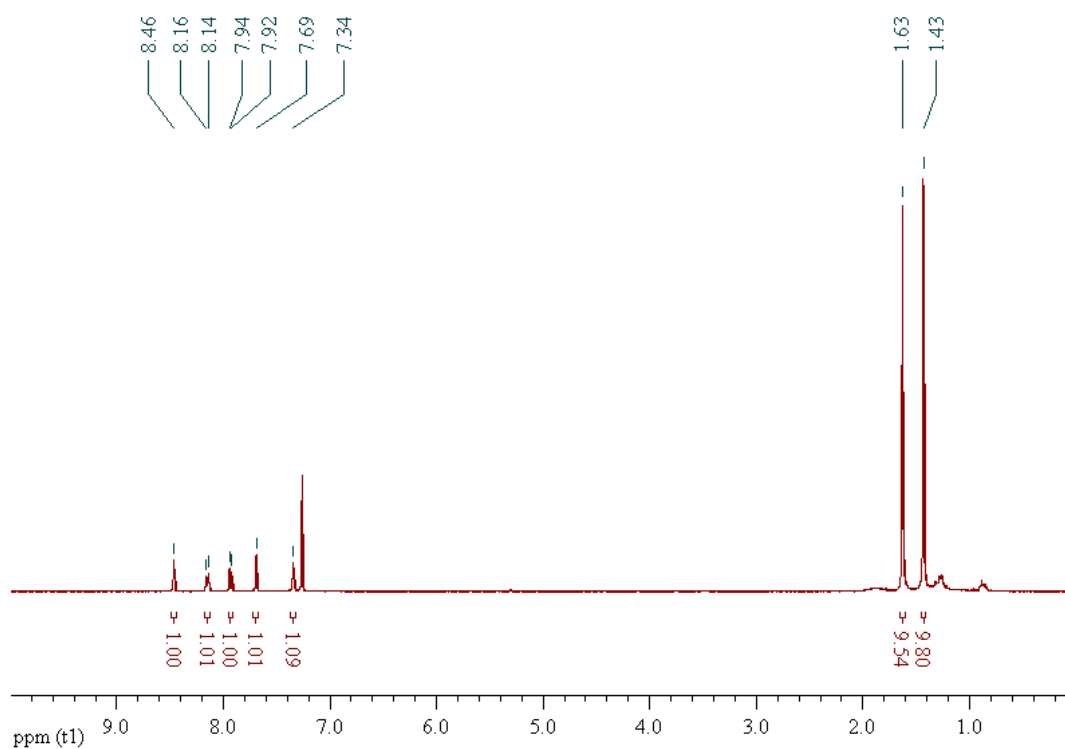
³¹P{¹H} NMR spectrum of 2,5-bis(4',6'-di-*tert*-butylbenzoxaphospholyl)thiophene (**3**)

$^{31}\text{P}\{^{1}\text{H}\}$ NMR spectrum of 2,5-bis(4',6'-di-*tert*-butylbenzoxaphospholyl)thiophene (**3**)
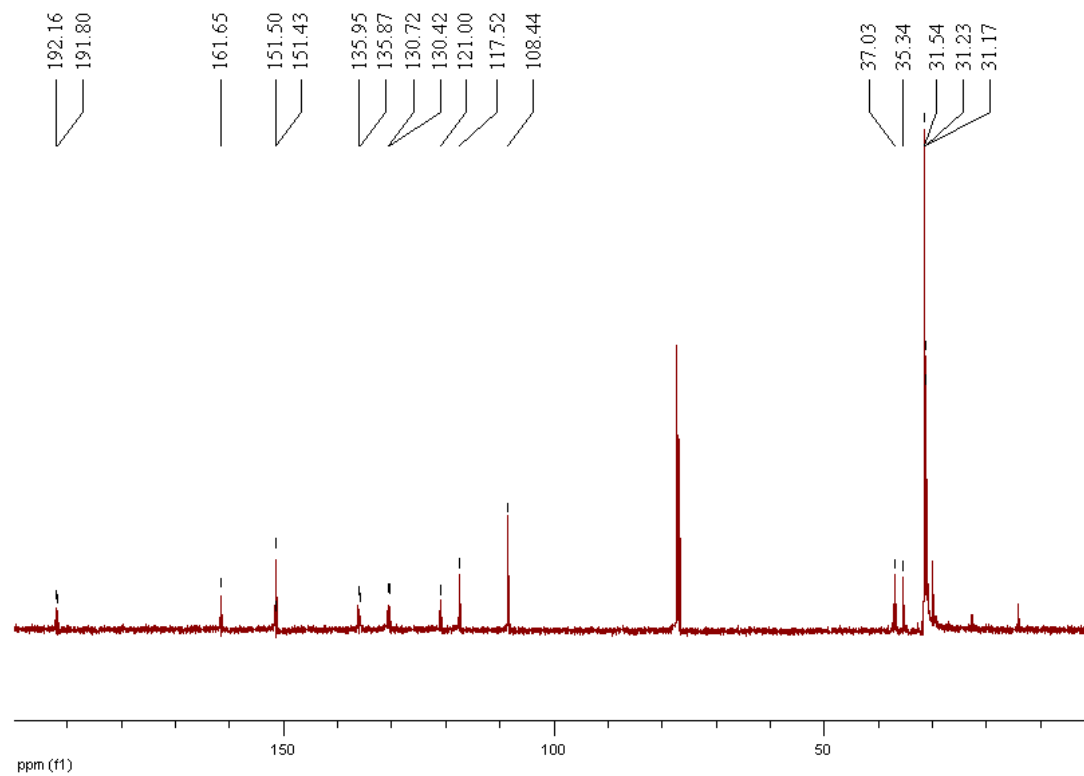

^{1}H NMR spectrum of 2,5-bis(4',6'-di-*tert*-butylbenzoxaphospholyl)thiophene (**3**)

¹³C{¹H} NMR spectrum of 2,5-bis(4',6'-di-*tert*-butylbenzoxaphospholyl)thiophene (**3**)

ppm (t1)

³¹P{¹H} NMR spectrum of 1,3,5-tris(4',6'-di-*tert*-butyl-benzoxaphospholyl)benzene (**4**)

ppm (t1)

¹H NMR spectrum of 1,3,5-tris(4',6'-di-*tert*-butyl-benzoxaphospholyl)benzene (**4**)

8.65
7.78
7.37
1.65
1.45

1.00
1.08
1.05
10.01
10.01
10.01
10.01

ppm (t1)　9.0　8.0　7.0　6.0　5.0　4.0　3.0　2.0　1.0

¹³C{¹H} NMR spectrum of 1,3,5-tris(4',6'-di-*tert*-butyl-benzoxaphospholyl)benzene (**4**)

192.16
191.80
161.65
151.50
151.43
135.95
135.87
130.72
130.42
121.00
117.52
108.44
37.03
35.34
31.54
31.23
31.17

ppm (f1)　150　100　50

5. UV-vis absorption and emission spectra

1 in hexanes
y=24967.95388+0.016
R^2=0.99971

1 in CH$_2$Cl$_2$
y=11305.3172x+0.01133
R^2=0.99982
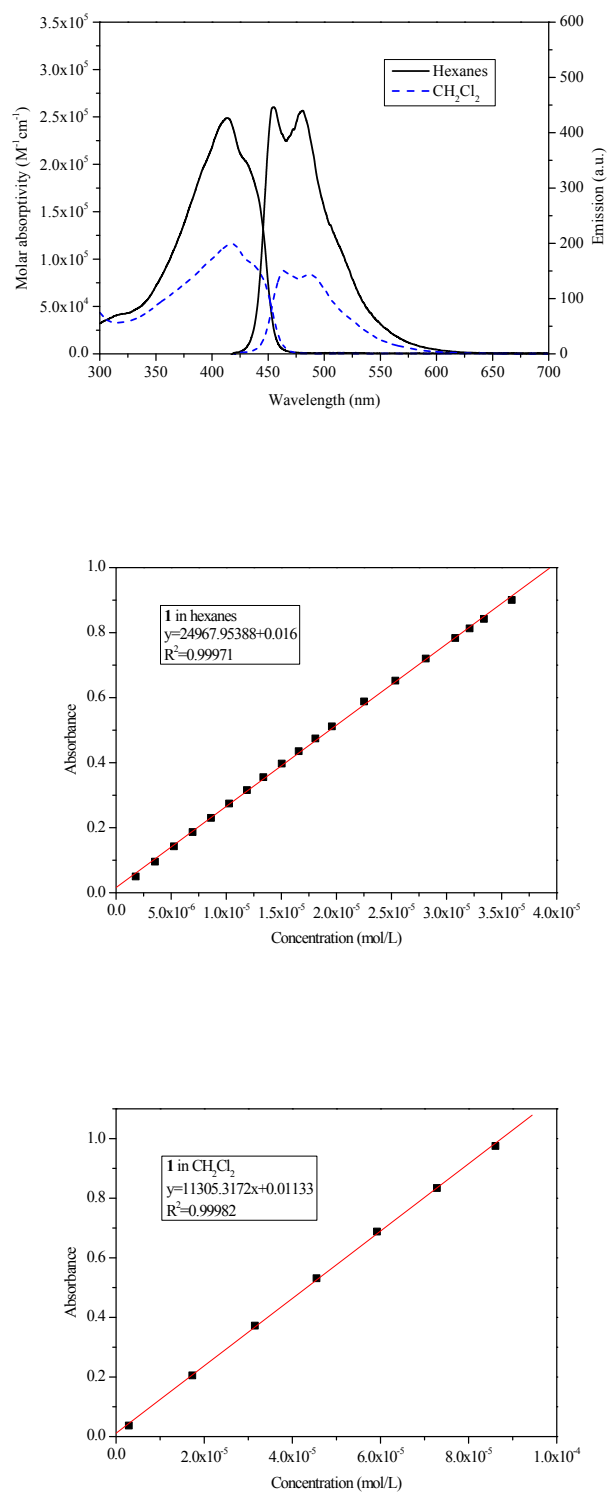
Figure S1 UV-vis absorption and fluorescence of **1** in hexanes and CH$_2$Cl$_2$ (Conc. 0.5×10^{-6} M，
top). Excitation wavelength for fluorescence measurements was the adsorption maxima. Beer's

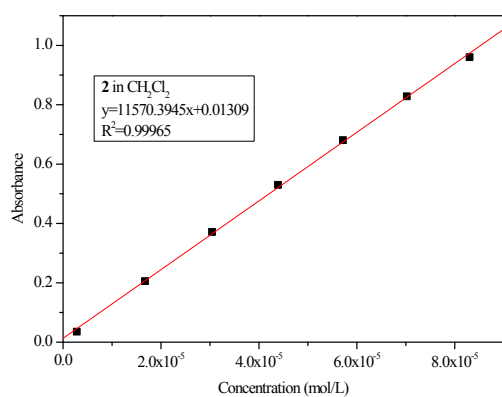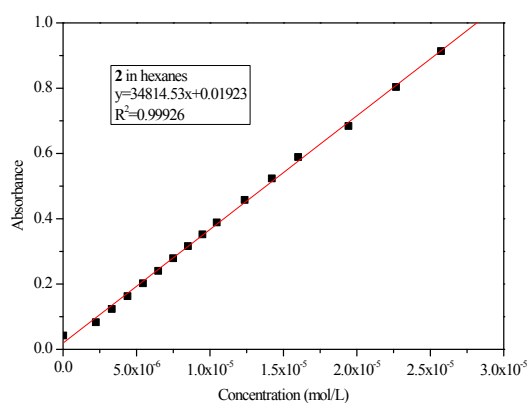law plots of **1** in hexanes (λ = 413 nm, middle) and CH$_2$Cl$_2$ (λ = 418 nm, bottom).

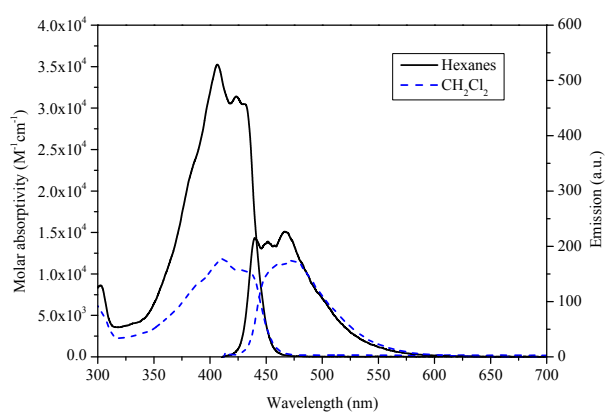**Figure S2** UV-vis absorption and fluorescence of **2** in hexanes and CH$_2$Cl$_2$ (Conc. 0.5×10^{-6} M，top). Excitation wavelength for fluorescence measurements was the adsorption maxima. Beer's law plots of **2** in hexanes (λ = 407 nm, middle) and CH$_2$Cl$_2$ (λ = 412 nm, bottom).
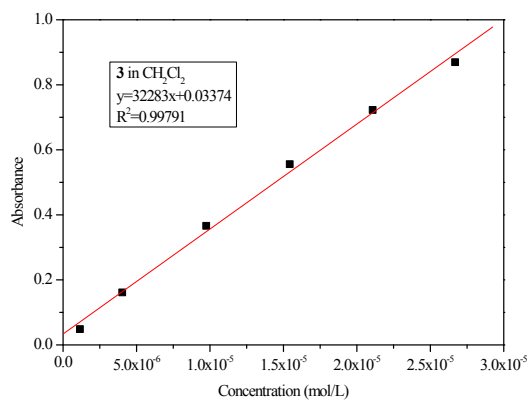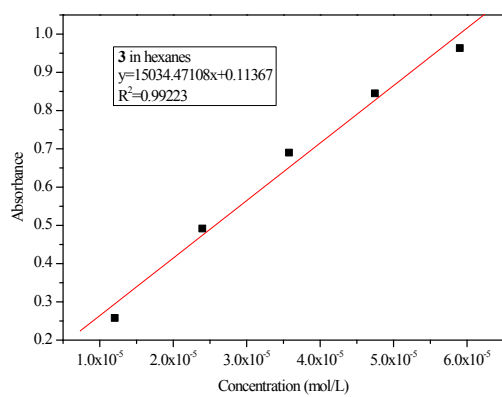
Figure S3 UV-vis absorption and fluorescence of **3** in hexanes and CH$_2$Cl$_2$ (Conc. 0.5×10^{-6} M，top). Excitation wavelength for fluorescence measurements was the adsorption maxima. Beer's law plots of **3** in hexanes (λ = 452 nm, middle) and CH$_2$Cl$_2$ (λ = 457 nm, bottom).
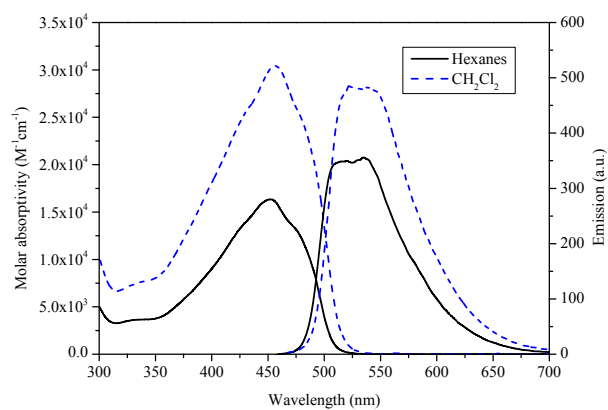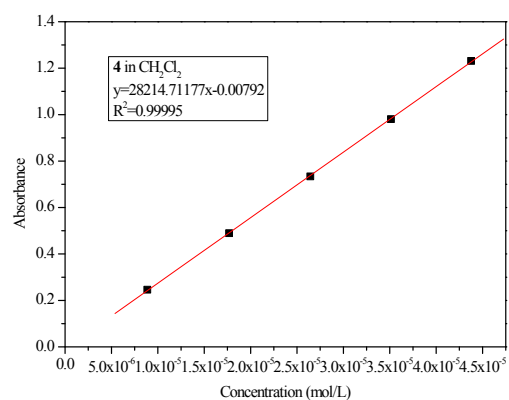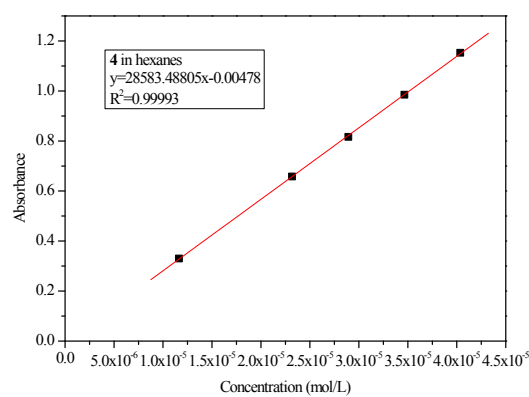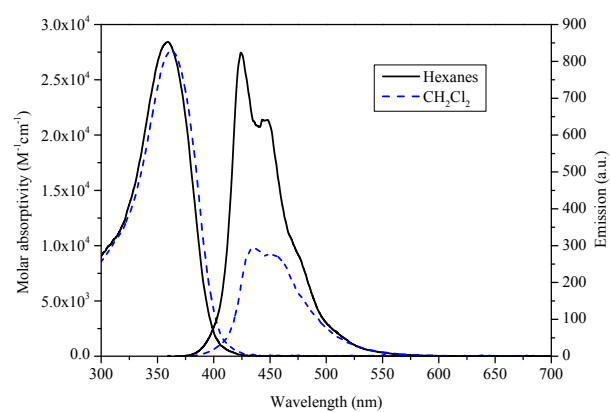
Figure S4 UV-vis absorption and fluorescence of **4** in hexanes and CH$_2$Cl$_2$ (Conc. 2.5×10^{-6} M，top). Excitation wavelength for fluorescence measurements was the adsorption maxima. Beer's law plots of **4** in hexanes (λ = 359 nm, middle) and CH$_2$Cl$_2$ (λ = 362 nm, bottom).

6. DFT calculation

A. A series of DFT calculations (B3LYP 6-31G*) were conducted using Spartan '10 (Wavefunction, Inc., Irvine, CA) to minimize several possible conformations of the compounds.

i. For the compound **1**, two structures were minimized. The energy difference was only 0.00021 au (ca 0.1 kcal/mol), favoring the "*trans*" species.

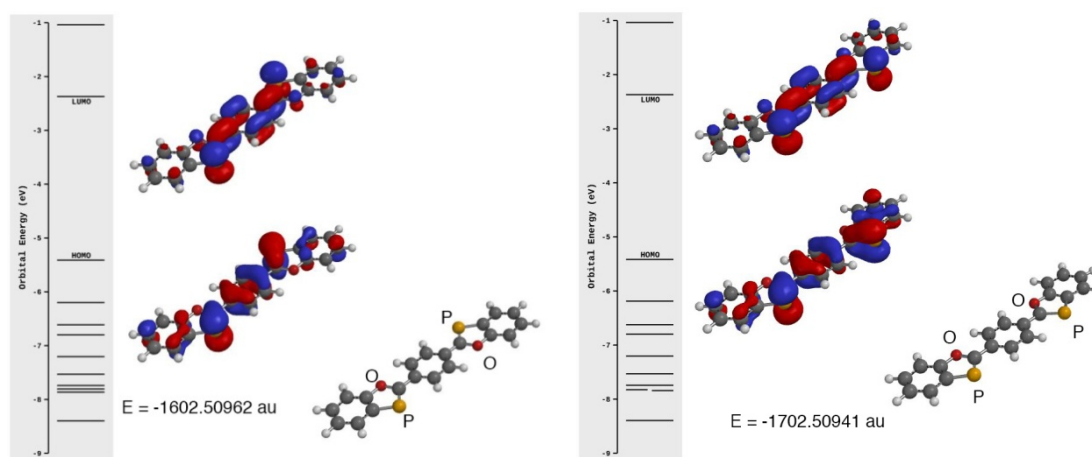**Figure S5** MO diagram for "*trans*" (left) and "*cis*" (right) isomers of **1** ($d_{P=C}$ = 1.737Å).

ii. For the compound **3**, three possible structures were minimized. The lowest energy was the "*cis*" species having the oxygen atoms nearest to the sulfur atom.
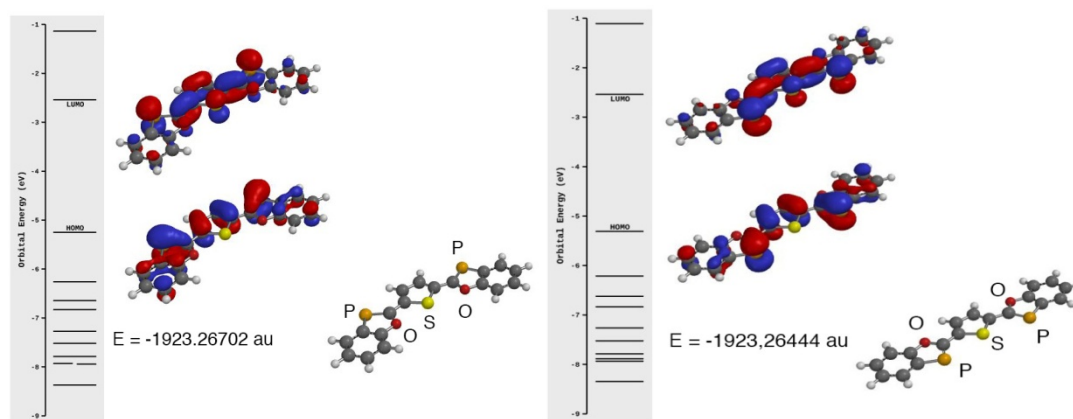

Figure S6 MO diagrams for "*cis* OSO" (left, $d_{P=C}$ = 1.741Å) and "*trans* PSP" (right, $d_{P=C}$ = 1.738 Å) isomers of **3**.

B. The two lowest energy structures from the 6-31G* calculations (Spartan '10, Wavefunction, Inc., Irvine, CA) were then subjected to further refinement using DFT B3LYP 6-311+(d,p) Gaussian 09, Revision **D.01**.[4] Following these optimizations, single point energy calculations were undertaken TDDFT CAM-B3LYP 6-311G+(d,p) using IEFPCM solvent correction (CH_2Cl_2).

i. "*trans*" isomer of 1

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	1	0	6.953335	-2.109129	-0.069879
2	6	0	6.638577	-1.072031	-0.042869
3	6	0	5.840941	1.642912	0.027571
4	6	0	5.271047	-0.747303	-0.032996
5	6	0	7.581021	-0.054411	-0.017779
6	6	0	7.185305	1.293862	0.017036
7	6	0	4.912281	0.607024	0.002366
8	1	0	8.636773	-0.299591	-0.025235
9	1	0	7.938209	2.073064	0.036011
10	1	0	5.516108	2.675701	0.054380
11	15	0	3.798510	-1.781492	-0.056789
12	6	0	2.852501	-0.330334	-0.018154
13	8	0	3.566947	0.834796	0.010646
14	6	0	1.407726	-0.158931	-0.009542
15	6	0	-1.407726	0.158931	0.009542
16	6	0	0.551397	-1.274103	-0.053247
17	6	0	0.823410	1.121861	0.043583
18	6	0	-0.551397	1.274103	0.053247
19	6	0	-0.823410	-1.121861	-0.043583
20	1	0	0.971733	-2.272541	-0.096129
21	1	0	1.460017	1.995800	0.078506
22	1	0	-0.971733	2.272541	0.096129
23	1	0	-1.460017	-1.995800	-0.078506
24	6	0	-2.852501	0.330334	0.018154
25	15	0	-3.798510	1.781492	0.056789
26	6	0	-5.271047	0.747303	0.032996
27	6	0	-7.185305	-1.293862	-0.017036
28	6	0	-4.912281	-0.607024	-0.002366
29	6	0	-6.638577	1.072031	0.042869
30	6	0	-7.581021	0.054411	0.017779
31	6	0	-5.840941	-1.642912	-0.027571
32	1	0	-6.953335	2.109129	0.069879
33	1	0	-8.636773	0.299591	0.025235

34	1	0	-5.516108	-2.675701	-0.054380
35	1	0	-7.938209	-2.073064	-0.036011
36	8	0	-3.566947	-0.834796	-0.010646

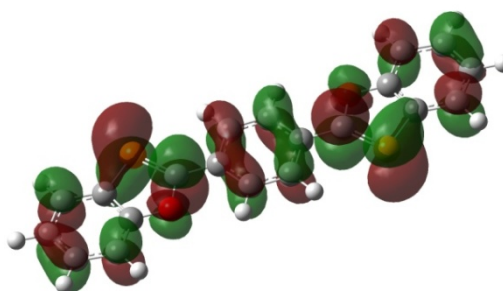
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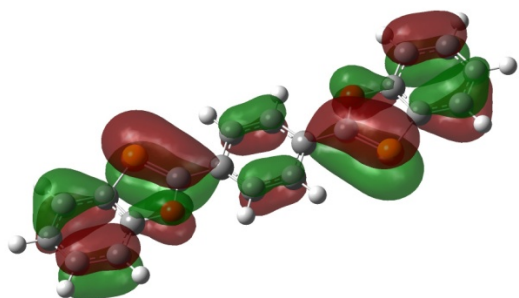
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#88
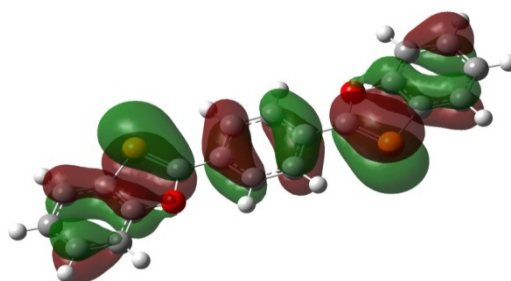
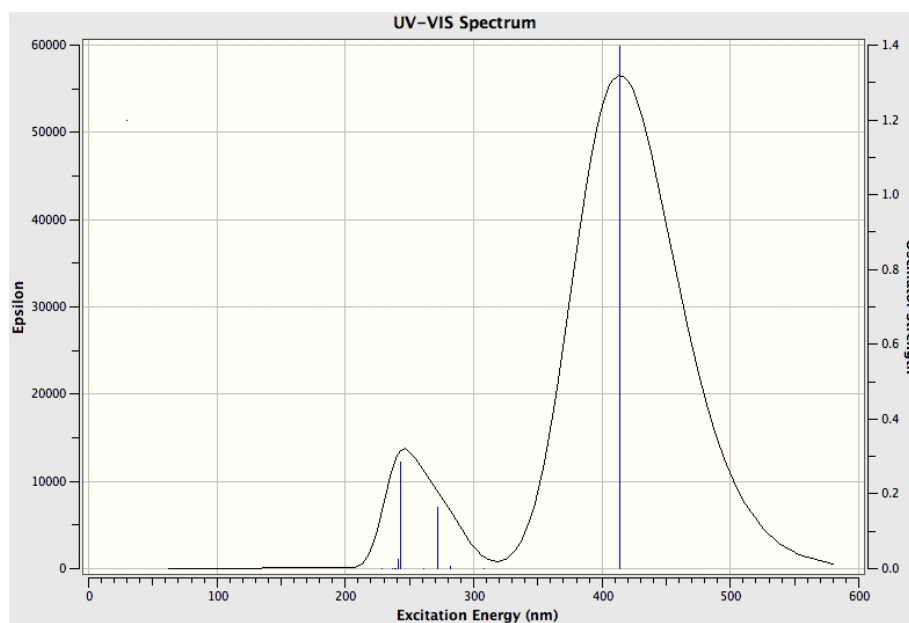HOMO
 #89
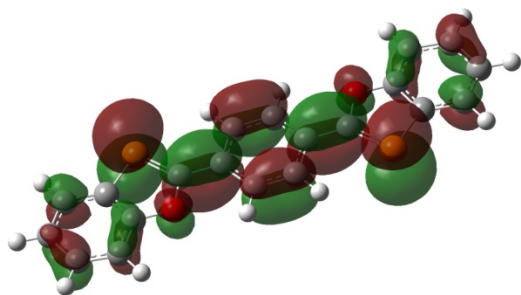
LUMO
#90

LUMO(+1)
 #91

Excitation energies and oscillator strengths:

Excited State 1:   Singlet-AU   2.9949 eV   413.99 nm   f=1.3973   <S**2>=0.000
    88 -> 91   -0.12139
    89 -> 90   0.68772
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-KS) = -1602.16657322
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2:   Singlet-AG   4.0249 eV   308.04 nm   f=0.0000   <S**2>=0.000
    88 -> 90   0.62369
    89 -> 91   -0.29120

Excited State 3:   Singlet-AU   4.3931 eV   282.23 nm   f=0.0067   <S**2>=0.000
    85 -> 90   0.45284
    87 -> 90   -0.35253
    89 -> 92   0.33469
    89 -> 93   0.12484

Excited State 4:   Singlet-AU   4.5549 eV   272.20 nm   f=0.1652   <S**2>=0.000
    85 -> 90   0.29342
    86 -> 91   -0.19927
    87 -> 90   0.51481
    88 -> 91   0.12552
    89 -> 92   0.17698
    89 -> 99   0.15778

Excited State 5:   Singlet-AG   4.5559 eV   272.14 nm   f=0.0000   <S**2>=0.000
    86 -> 90   -0.40769
    87 -> 91   0.22403
    88 -> 90   0.22365
    89 -> 91   0.42733

Excited State 6:   Singlet-AG   4.7451 eV   261.29 nm   f=0.0000   <S**2>=0.000
    84 -> 91   0.11990
    86 -> 90   0.43929
    87 -> 91   -0.13454
    88 -> 90   0.18148
    89 -> 91   0.44434
    89 -> 97   0.11426

Excited State 7:   Singlet-AU   5.0981 eV   243.20 nm   f=0.2835   <S**2>=0.000
    85 -> 90   -0.37109
    88 -> 94   0.14594

89 -> 92	0.55418				

Excited State   8:   Singlet-AU   5.1371 eV   241.35 nm   f=0.0239   <S**2>=0.000

81 -> 91	-0.28656
82 -> 90	0.62505

Excited State   9:   Singlet-AU   5.1822 eV   239.25 nm   f=0.0012   <S**2>=0.000

84 -> 90	0.17149
86 -> 94	-0.15741
87 -> 90	0.11080
87 -> 99	0.13532
88 -> 91	0.18255
88 -> 94	-0.14961
88 -> 97	-0.22276
89 -> 93	0.47709
89 -> 99	-0.16225

Excited State 10:   Singlet-AG   5.2021 eV   238.34 nm   f=0.0000   <S**2>=0.000

81 -> 90	0.61268
82 -> 91	-0.31132

Excited State 11:   Singlet-AG   5.2445 eV   236.41 nm   f=0.0000   <S**2>=0.000

86 -> 93	-0.11196
87 -> 97	-0.10832
88 -> 93	-0.28270
88 -> 99	0.11117
89 -> 94	0.55869
89 -> 97	0.13843

Excited State 12:   Singlet-AG   5.4298 eV   228.34 nm   f=0.0000   <S**2>=0.000

88 -> 96	-0.18050
88 ->102	0.10115
89 -> 95	0.61184
89 -> 98	0.11199
89 ->104	0.11953

ii. "*cis* OSO" isomer of 3

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z

Center Number	Atomic Number	Atomic Type	X	Y	Z
1	1	0	0.000000	7.104565	-0.860487
2	6	0	0.000000	6.433804	-0.008789
3	6	0	0.000000	4.702926	2.230941
4	6	0	0.000000	5.041861	-0.204143
5	6	0	0.000000	6.941304	1.282580
6	6	0	0.000000	6.082597	2.394869
7	6	0	0.000000	4.215908	0.928492
8	1	0	0.000000	8.014010	1.437634
9	1	0	0.000000	6.500168	3.394819
10	1	0	0.000000	4.023521	3.074214
11	15	0	0.000000	4.051464	-1.708153
12	6	0	0.000000	2.641306	-0.695333
13	8	0	0.000000	2.878118	0.651476
14	6	0	0.000000	1.252903	-1.055912
15	6	0	0.000000	0.701124	-2.328052
16	1	0	0.000000	1.301990	-3.227882
17	6	0	0.000000	-0.701124	-2.328052
18	1	0	0.000000	-1.301990	-3.227882
19	6	0	0.000000	-1.252903	-1.055912
20	16	0	0.000000	0.000000	0.165534
21	6	0	0.000000	-2.641306	-0.695333
22	8	0	0.000000	-2.878118	0.651476
23	6	0	0.000000	-4.215908	0.928492
24	6	0	0.000000	-6.941304	1.282580
25	6	0	0.000000	-4.702926	2.230941
26	6	0	0.000000	-5.041861	-0.204143
27	6	0	0.000000	-6.433804	-0.008789
28	6	0	0.000000	-6.082597	2.394869
29	1	0	0.000000	-4.023521	3.074214
30	1	0	0.000000	-7.104565	-0.860487
31	1	0	0.000000	-6.500168	3.394819
32	1	0	0.000000	-8.014010	1.437634
33	15	0	0.000000	-4.051464	-1.708153

-
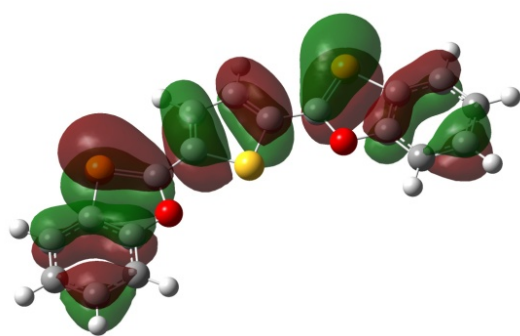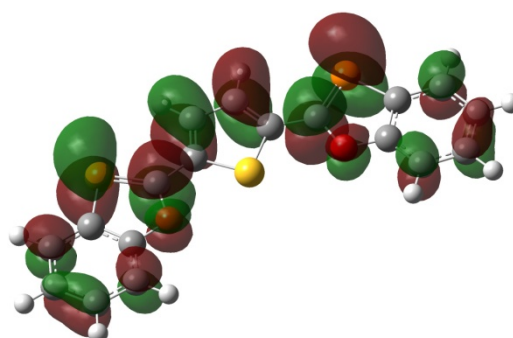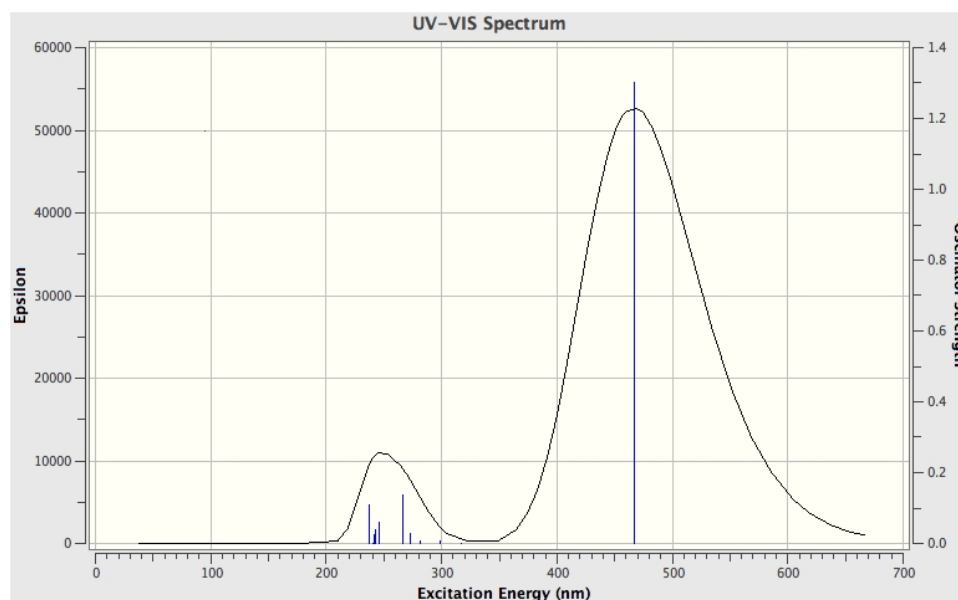
HOMO(-1)
#89
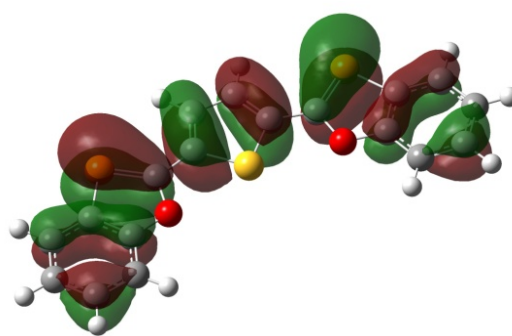
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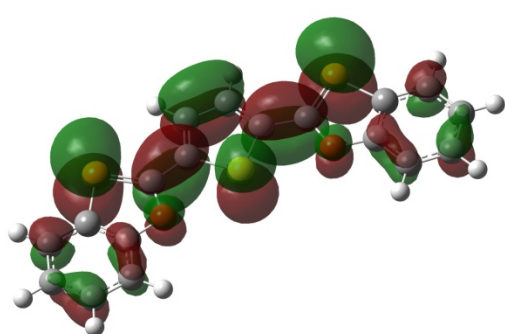
LUMO
#91

LUMO(+1)
#92

Excitation energies and oscillator strengths:

Excited State 1:   Singlet-B2   2.6566 eV   466.71 nm   f=1.3020   <S**2>=0.000

90 -> 91   0.69358

This state for optimization and/or second-order correction.

Total Energy, E(TD-HF/TD-KS) = -1922.98305625

Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2:   Singlet-A1   3.9125 eV   316.89 nm   f=0.0000   <S**2>=0.000
         89 -> 91   0.58985
         90 -> 92   -0.35709

Excited State 3:   Singlet-A1   4.1536 eV   298.50 nm   f=0.0053   <S**2>=0.000
         86 -> 91   0.21368
         87 -> 91   -0.13459
         88 -> 92   0.10528
         89 -> 91   0.33619
         90 -> 92   0.53201

Excited State 4:   Singlet-B2   4.3988 eV   281.86 nm   f=0.0062   <S**2>=0.000
         87 -> 92   -0.18002
         88 -> 91   0.64089
         89 -> 92   0.13068
         90 -> 97   0.11101

Excited State 5:   Singlet-A1   4.5485 eV   272.58 nm   f=0.0282   <S**2>=0.000
         85 -> 92   0.10535
         86 -> 91   -0.18201
         87 -> 91   0.58727
         88 -> 92   -0.15668
         90 -> 92   0.20665
         90 -> 98   0.11418

Excited State 6:   Singlet-A1   4.6589 eV   266.12 nm   f=0.1358   <S**2>=0.000
         86 -> 91   0.62877
         87 -> 91   0.17608
         88 -> 92   -0.10869
         90 -> 92   -0.12917

Excited State 7:   Singlet-B2   5.0448 eV   245.77 nm   f=0.0579   <S**2>=0.000
         85 -> 91   -0.16342
         87 -> 94   0.14333
         88 -> 97   -0.12510
         89 -> 92   -0.15929
         89 -> 94   0.16863
         89 -> 98   0.15921
         90 -> 93   0.54700

90 -> 97	0.14587

Excited State 8: Singlet-A1   5.0985 eV   243.18 nm   f=0.0383   <S**2>=0.000

87 -> 93	0.12821
89 -> 93	0.25079
90 -> 94	0.59843
90 -> 98	0.11344

Excited State 9: Singlet-B1   5.1312 eV   241.63 nm   f=0.0241   <S**2>=0.000

82 -> 92	-0.27935
83 -> 91	0.62606

Excited State 10: Singlet-A2   5.1321 eV   241.59 nm   f=0.0000   <S**2>=0.000

82 -> 91	0.37703
83 -> 92	-0.17314
90 -> 95	0.48313
90 -> 99	-0.21772

Excited State 11: Singlet-A2   5.1527 eV   240.62 nm   f=0.0000   <S**2>=0.000

82 -> 91	0.49467
83 -> 92	-0.22640
90 -> 95	-0.33195
90 -> 99	0.23915

Excited State 12: Singlet-B2   5.2143 eV   237.78 nm   f=0.1104   <S**2>=0.000

85 -> 91	0.35356
87 -> 92	0.11880
88 -> 91	0.12448
88 -> 93	-0.13416
89 -> 92	0.10407
89 -> 94	0.21066
89 -> 98	-0.17560
90 -> 93	0.30670
90 -> 97	-0.33905

7. References

1. (a)A. M. C. H. van den Nieuwendijk, D. Pietra, L. Heitman, A. Göeblyös and A. P. IJzerman, *J. Med. Chem.*, 2004, **47**, 663-672. (b)R. Seto, T. Kojima, K. Hosokawa, Y. Koyama, G. Konishi and T. Takata, *Polymer*, 2010, **51**, 4744-4749.
2. S. Wu, N. Deligonal and J. D. Protasiewicz, *Dalton. Trans.*, 2013, **42**, 14866-14874.
3. J. N. Demas and G. A. Crosby, *J. Phys. Chem.*, 1971, **75**, 991-1024.
4. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian 09 (Revision D.01), Gaussian Inc., Wallingford, CT, 2009.