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A short pyrene-fused pyrazaacene with red to near-infrared photoluminescence

Raúl García,[a] *Manuel Melle-Franco,*[b] *and Aurelio Mateo-Alonso**[a,c]

[a]*POLYMAT, University of the Basque Country UPV/EHU, Avenida de Tolosa 72, E-20018 Donostia-San Sebastian, Spain. E-mail: amateo@polymat.eu*
[b]*Centro ALGORITMI, Universidade do Minho, 4710-057 Braga, Portugal*
[c]*Ikerbasque, Basque Foundation for Science, Bilbao, Spain*

1. General methods

Reagents for synthesis were used as purchased. Nitrogen was used as inert atmosphere when necessary. Column chromatography was carried out using silica gel (40-63 µm) from Fluka. Analytical thin layer chromatography (TLC) was done using aluminium sheets (20x20 cm) pre-coated with silica gel RP-18W 60 F254 from Merck, or aluminium foils (20x20 cm) covered with nano-silica gel from Fluka. UV active compounds were detected with a UV lamp from CAMAG at wavelength λ = 254 or 366 nm.

NMR spectra were recorded on Bruker Avance 400 spectrometer at 298 K using partially deuterated solvents as internal standards. Coupling constants (*J*) are denoted in Hz and chemical shifts (*δ*) in ppm. Multiplicities are denoted as follows: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad.

Matrix Assisted Laser Desorption Ionization (coupled to a Time-Of-Flight analyzer) experiments (MALDI-TOF) were recorded on Bruker AutoFlex Speed spectrometer by Dr. Antonio Veloso (POLYMAT).

Absorption and emission spectra were recorded on a Perkin Elmer Lambda 950 UV-Vis-NIR spectrophotometer and a Perkin Elmer LS55 fluorescence spectrophotometer, respectively.

Electrochemical measurements were carried out on a Princeton Applied Research Parstat 2273 in a 3-electrode single compartment cell with Pt disc working electrode (Ø = 0.5 mm), a platinum wire counter electrode (Ø = 0.5 mm) and a silver wire pseudoreference electrode. The cell and the electrodes were custom made. The reduction potentials were referred to SCE using ferrocene (Fc) as internal reference ($E_{1/2\ Fc}^{SCE}$ =+0.48 V) after the measurements. Anhydrous THF was dried using a Innovative Pure Solve solvent purification system.

2. Synthesis and characterization of compounds 3-6.

Compound 3

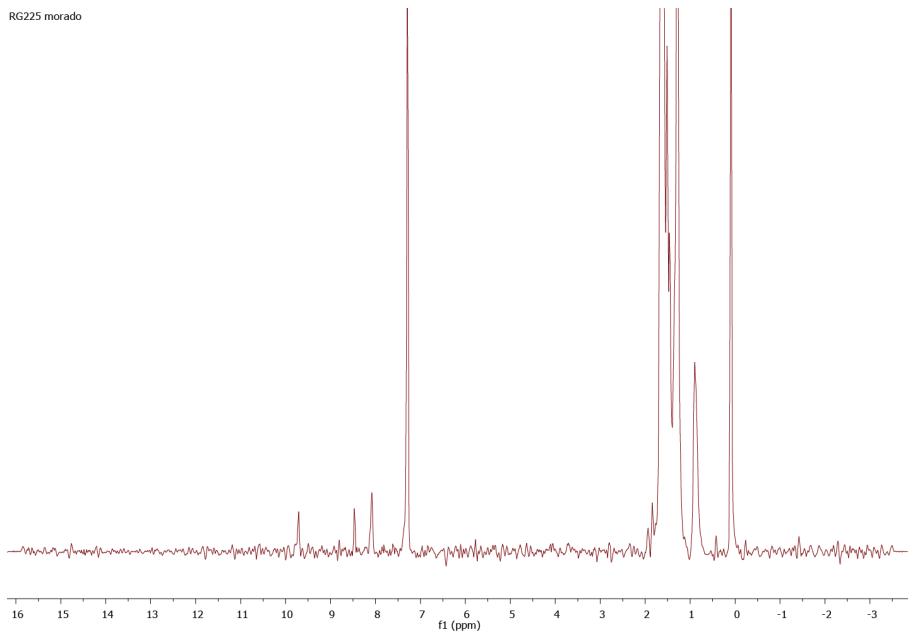
2,7-Di-*tert*-butylpyrene-4,5-dione (100 mg, 0.3 mmol) and 2,3-diaminomaleonitrile (98 mg, 0.9 mmol) are dissolved in 30 mL of glacial acetic acid, and the mixture is heated to reflux and allowed to stir for 72 h. After cooling to room temperature, the solvent is removed under vacuum, and the crude product is purified by column chromatography (silica gel, dichloromethane as eluent) to afford the product as a purple solid with a 66% yield. Since compound **3** has a large tendency to aggregate, a saturated solution of **3** in $CDCl_3$ was diluted ~10 times that showed resolved signals corresponding to its structure with no signs of aggregation. The low concentration did not allow the acquisition of the ^{13}C NMR spectra in this solvent and thus it was carried out in pyridine-d_5 with satisfactory results.

^1H NMR ($CDCl_3$, 400 MHz) δ: 9.71 (s, 2H), 8.45 (s, 2H), 8.08 (s, 2H), 1.67 (s, 18H)

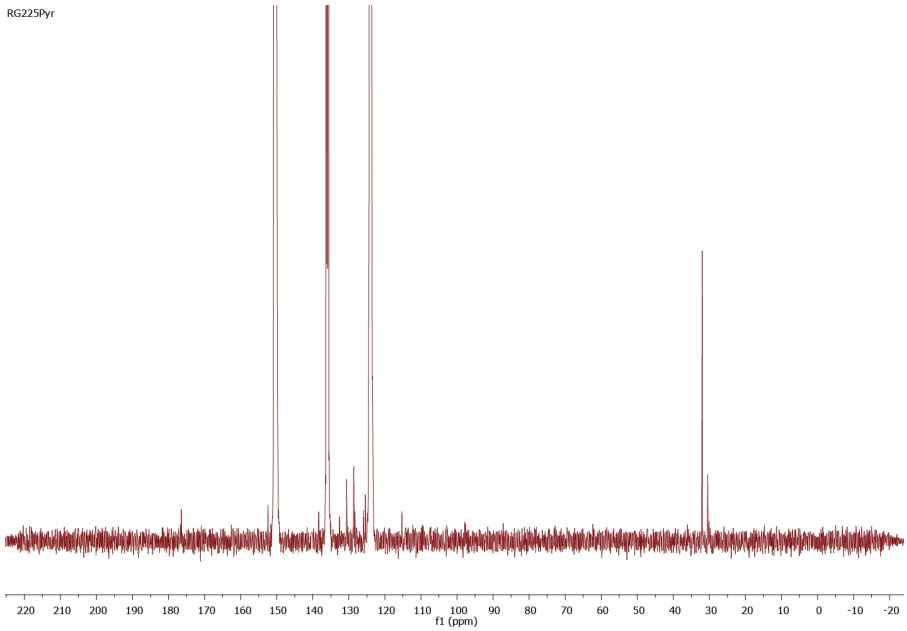
^{13}C NMR (pyridine-d_5, 100 MHz) δ: 176.5, 152.4, 138.4, 132.6, 130.6, 128.6, 128.3, 125.9, 125.4, 115.3, 32.0, 30.4

MS (MALDI) *m/z*: calculated for $[M+H]^+$ ($C_{30}H_{24}N_6$) = 469.21, found = 469.21

UV-Vis (DCM) λ (log ε): 271 (4.37), 299 (4.24), 354 (4.31), 366 (4.47), 571 (3.94)



^1H NMR spectrum ($CDCl_3$, 400 MHz) of compound **3**.



^{13}C NMR spectrum (pyridine-d_5, 100 MHz) of compound **3**.

Compound 4

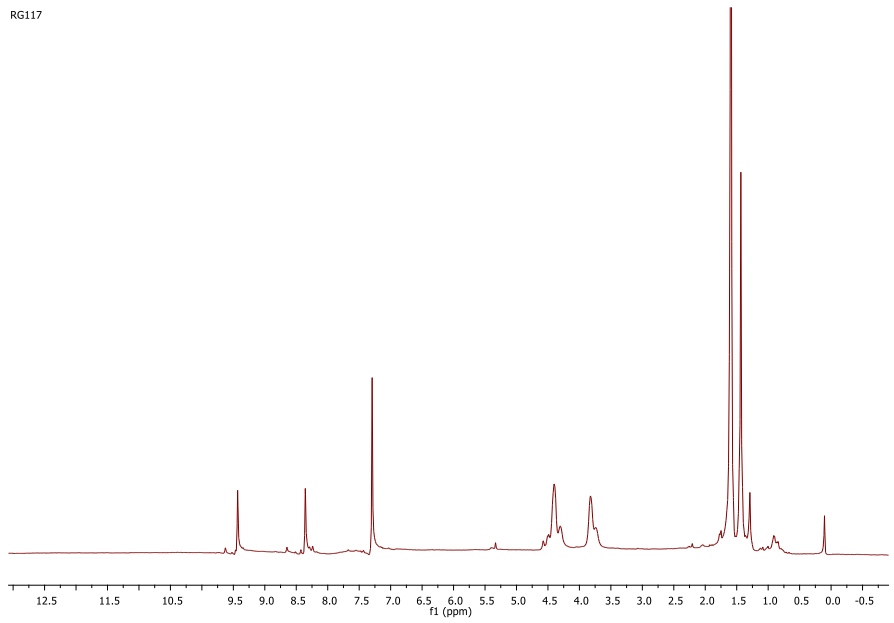
In a dry, argon flushed Schlenk flask, pyrene-2,7-di-*tert*-butyl-4,5-dione-9,10-di(ethylenglycol)ketal (50 mg, 0.12 mmol) and 4,5-diamino-2,3-dicyanopyrazine (58 mg, 0.36 mmol) were dissolved in degassed AcOH. The reaction mixture was heated to reflux and stirred for 16 h, then cooled to room temperature and the solvent was removed under vaccum. The crude product was purified by column chromatography, using dichloromethane as eluent. Yield: 52%

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 9.43 (s, 2H), 8.36 (s, 2H), 4.40 (bs, 4H), 3.82 (bs, 4H), 1.59 (s, 18H)

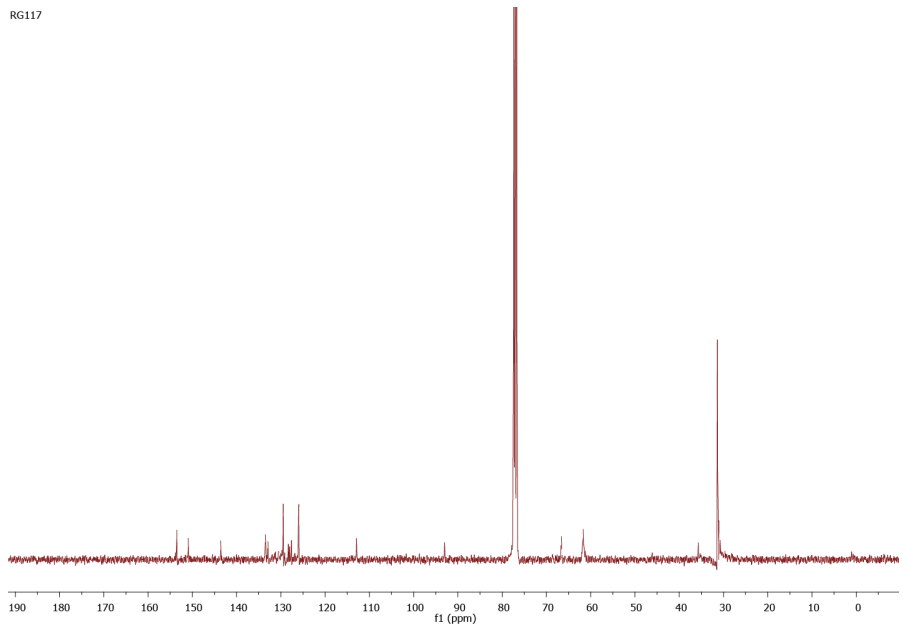
^{13}C NMR ($CDCl_3$, 100 MHz) δ: 153.5, 150.9, 143.6, 133.5, 132.9, 129.5, 128.2, 127.6, 126.0, 112.9, 93.0, 67.6, 66.7, 35.7, 31.4

MS (MALDI) *m/z*: calculated for $[M+H]^+$ ($C_{34}H_{31}N_6O_4$) = 587.233; found = 587.471

UV-Vis (DCM) λ (log ε): 351 (4.25), 445 (4.23)



^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of compound **4**.



^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of compound **4**.

Compound 5

2,7-Di-*tert*-butylpyrene-4,5-dione (100 mg, 0.3 mmol) and 2,3-diaminomaleonitrile (98 mg, 0.9 mmol) are dissolved in 30 mL of glacial acetic acid, and the mixture is heated to reflux and allowed to stir for 72 h. After cooling to room temperature, the solvent is removed under vacuum, and the crude product is

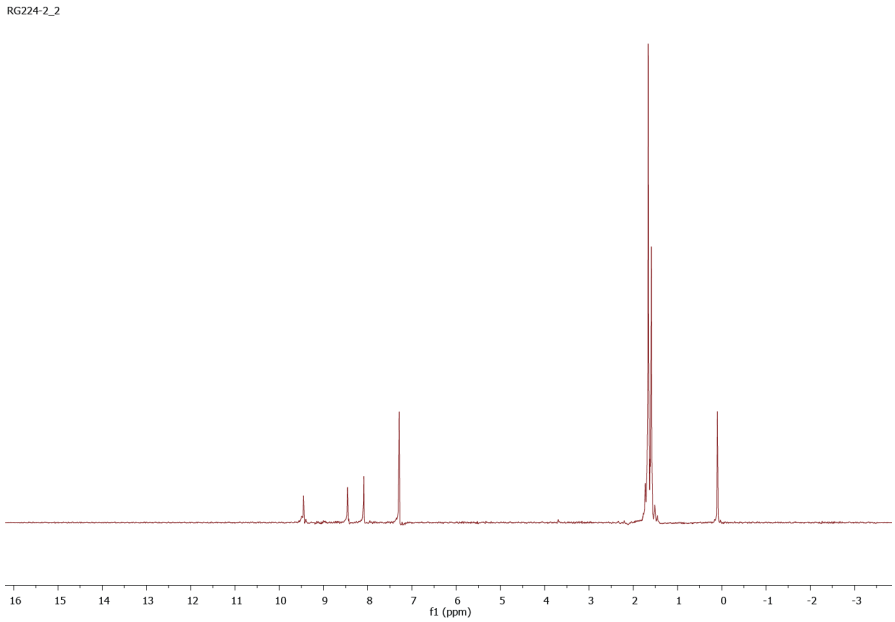
purified by column chromatography (silica gel, dichloromethane as eluent) to afford the product as a pale orange solid with a 65% yield.

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 9.45 (s, 2H), 8.45 (s, 2H), 8.09 (s, 2H), 1.66 (s, 18H)

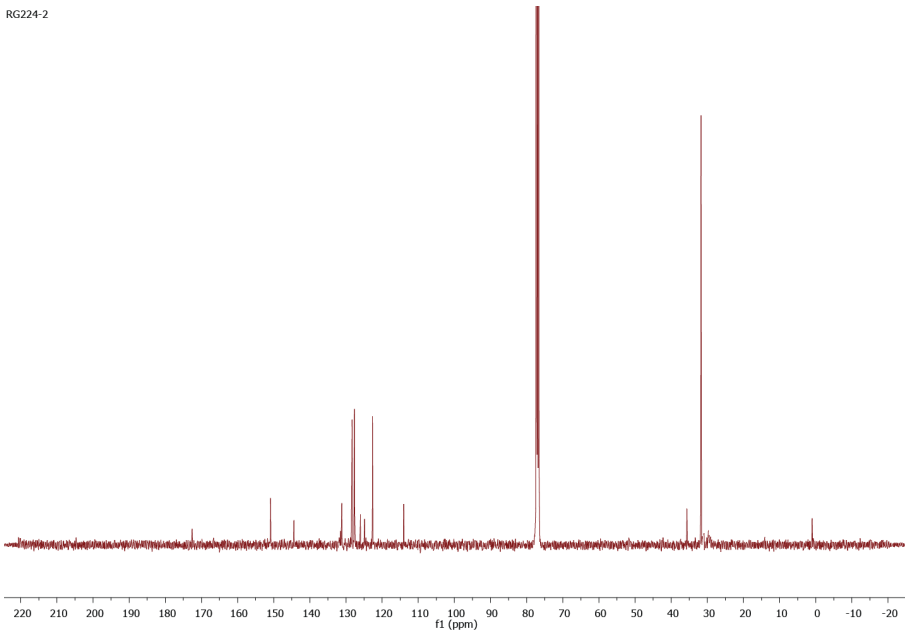
^{13}C NMR ($CDCl_3$, 100 MHz) δ: 172.6, 150.9, 144.4, 131.2, 128.3, 127.6, 126.0, 124.9, 122.7, 114.0, 35.7, 31.7

MS (MALDI) *m/z*: calculated for $[M]^+$ ($C_{28}H_{24}N_4$) = 416.2, found = 416.1

UV-Vis (DCM) λ (log ε): 285 (4.21), 316 (3.85), 347 (3.84), 364 (3.93), 455 (3.44).



^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of compound **5**.



^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of compound **5**.

Compound 6

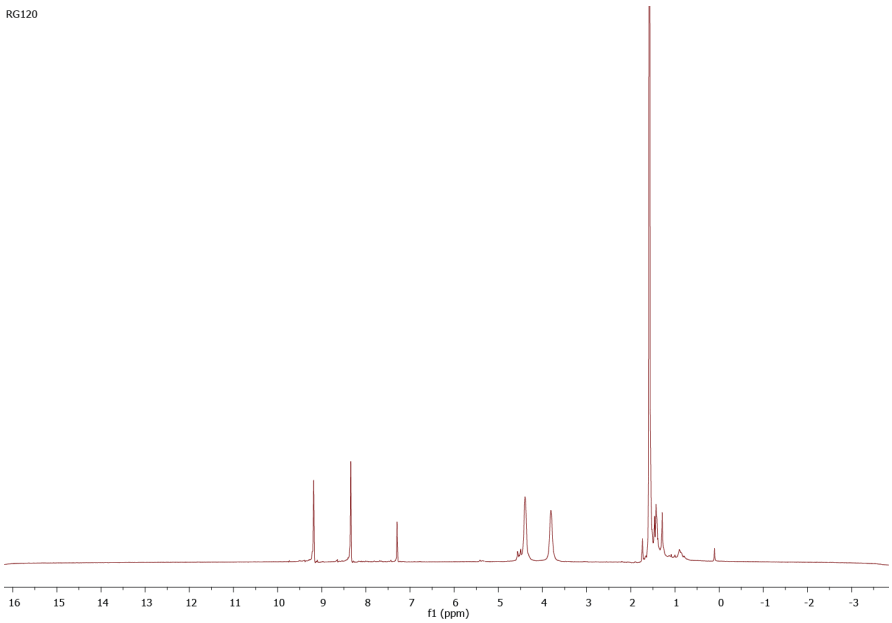
In a dry, argon flushed Schlenk flask, pyrene-2,7-di-*tert*-butyl-4,5-dione-9,10-di(ethylenglycol)ketal (50 mg, 0.12 mmol) and diaminomaleonitrile (38 mg, 0.36 mmol) were dissolved in degassed AcOH. The reaction mixture was heated to reflux and stirred for 48 h, then cooled to room temperature and the solvent was removed under vaccum. The crude product was purified by column chromatography, using dichloromethane as eluent. Yield: 43%

^{1}H NMR ($CDCl_3$, 400 MHz) δ: 9.18 (s, 2H), 8.34 (s, 2H), 4.40 (bs, 4H), 3.81 (bs, 4H), 1.58 (s, 18H)

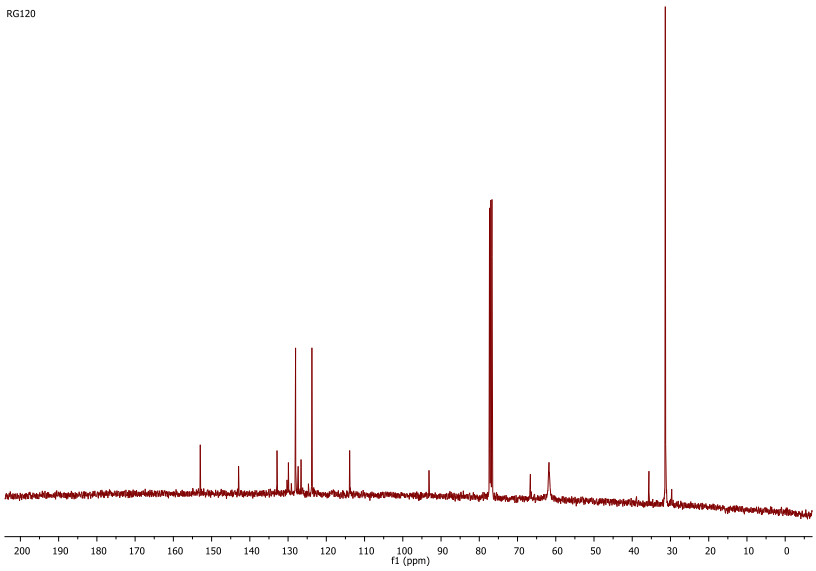
^{13}C NMR ($CDCl_3$, 100 MHz) δ: 153.0, 143.0, 132.9, 129.9, 128.0, 127.4, 126.6, 123.8, 113.9, 93.2, 66.6, 61.8, 35.6, 31.3

MS (MALDI) *m/z*: calculated for $[M+H]^+$ ($C_{32}H_{31}N_4O_4$) = 535.227; found = 535.459

UV-Vis (DCM) λ (log ε): 329 (4.43), 347 (4.45), 390 (3.98)



^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of compound **6**.



^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of compound **6**.

3. DFT calculations

The four compounds were studied with three DFT Hamiltonians: B3LYP, CAM-B3LYP and M06-2X. Geometries were minimized with the 6-31g(d,p) basis set and TD-DFT and orbital energies were computed with the 6-311+(2d,p) basis set. All minima were checked by frequency calculations. Calculations in vacuum and CH_2Cl_2 were performed for the B3LYP model and yielded very similar results, the data discussed was calculated with an implicit model of CH_2Cl_2.

The electronic spectra were calculated with TD-DFT. From TD-DFT all excited states are singlets (transitions involving triplets were found to be optically inactive), and the lowest energy electronic transition, i.e. first excitation, corresponds to HOMO->LUMO transitions. Calculations with the B3LYP Hamiltonian gave the absolute values more similar to experiment and are the only ones presented.

	B3LYP-CH_2Cl_2-6311g+(d2,p)/B3LYP-CH_2Cl_2-631(d,p)									
	exp LUMO	LUMO+1	LUMO	HOMO	HOMO-1	HOMO-2	DFT gap	1st Trans. TD-DFT/nm	1st Trans. TD-DFT/ev	opt. gap
3	-4.3	-3.0	-4.0	-6.3	-6.7	-7.6	2.3	633	2.0	1.9
4	-4.2	-3.0	-4.0	-6.6	-7.1	-7.1	2.6	623	2.0	2.2
5	-3.6	-3.0	-3.1	-6.2	-6.6	-7.8	3.1	482	2.6	2.1
6	-3.6	-3.0	-3.1	-6.5	-6.9	-7.2	3.4	454	2.7	2.8

Table S1. Energies of the different frontier orbitals.

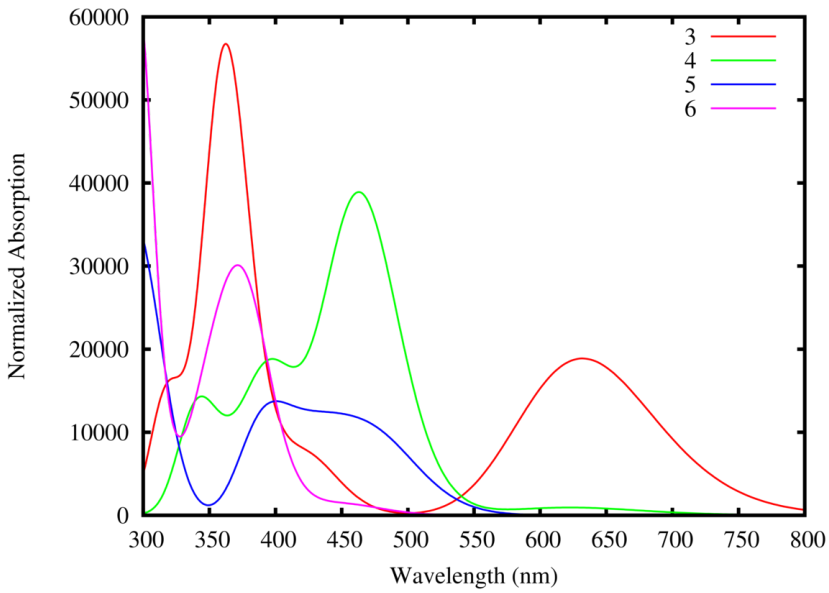


Figure S1. TD-B3LYP spectrum.