Supplementary Material (ESI) for Chemical Communications

Supporting Information

Bis-rhodium hexaphyrins: metalation of [28]hexaphyrin and a smooth Hückel aromatic-antiaromatic interconversion

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Instrumentation and Materials

^{1}H and ^{19}F NMR spectra were recorded on a JEOL ECA-600 spectrometer (600 MHz for ^{1}H and 565 MHz for ^{19}F). Chemical shifts were reported as delta scale in ppm relative to benzene-d_6 (δ = 7.20) for ^{1}H. Hexafluorobenzene was used as external reference for ^{19}F (δ = −162.9 ppm). UV-visible absorption spectra were recorded on a Shimadzu UV-3100PC spectrometer. IR spectra were recorded on a Horiba FT-710M. High-resolution ESI-TOF mass spectra were recorded on a BRUKER microTOF LC using ESI method in the positive or negative ion mode in acetonitrile solution. X-Ray data were taken on a Rigaku-Raxis imaging plate system, or on a BRUKER-APEX X-Ray diffractometer equipped with a large area CCD detector. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Silica gel column chromatography was performed on Wako-gel C-300. Thin-layer chromatography (TLC) was carried out on aluminum sheets coated with silica gel 60 F254 (Merck 5554). Dry dichloromethane was obtained by refluxing and distillation over CaH_2.

General Synthetic Procedure

*Preparation of **3***

Hexakis(pentafluorophenyl)[28]hexaphyrin **2** (70 mg, 47.9 μmol) was dissolved in 40 mL of CH_2Cl_2 in a round-bottomed flask, to this anhydrous sodium acetate (19 mg, 240 μmol, 5 equiv.) and 93 mg (239 μmol) $[RhCl(CO)_2]_2$ were added and the reaction mixture was refluxed under nitrogen atmosphere for 10-12 hrs. The reaction mixture was evaporated and loaded on silica gel column. A violet colour band was eluted with 40% CH_2Cl_2/hexane solvent. Subsequent evaporation and recrystallization from CH_2Cl_2/hexane gave 66 mg of **3** (78% yield).

^{1}H NMR (600 MHz, C_6D_6): δ [ppm] = 17.08 (s, 4H, inner β-H), 4.75 (d, J = 4.8 Hz, 4H, outer β-H), 3.68 (d, J = 4.8 Hz, 4H, outer β-H), 3.25 (s, 2H, outer NH); UV/vis(CH_2Cl_2): λ_{max} [nm] (ε [M^{-1} cm^{-1}]) = 395 (27000), 514 (108000), and 587 (97000); ESI-TOF-MS (negative mode): $C_{70}H_{13}F_{30}N_6O_4Rh_2$ ([M-H]$^-$): calcd: 1776.8624, found: 1776.8619.

*Preparation of **4** from **3***

20 mg (11.2 μmol) of **3** was dissolved in 10 mL CH_2Cl_2, to this was added 16 mg (67.5 μmol) of DDQ, the reaction mixture was stirred in air for 30 min. The reaction mixture was loaded on a short silica gel column and blue coloured solution was eluted from the column with complete CH_2Cl_2 as eluent. Evaporation and recrystallization of the solution from CH_2Cl_2/hexane gave 19.2 mg **4** in quantitative yield.

^{1}H NMR (600 MHz, C_6D_6): δ [ppm] = 9.41 (d, J = 4.1 Hz, 4H, outer β-H), 8.90 (d, J = 4.8 Hz, 4H, outer β-H), -3.97 (s, 4H, inner β-H); UV/vis(CH_2Cl_2): λ_{max} [nm] (ε [M^{-1} cm^{-1}]) = 353 (41000), 579 (216000), 605 (200000), 755 (24000), 827 (21300), and 942 (1400); ESI-TOF-MS (positive mode): $C_{70}H_{13}F_{30}N_6O_4Rh_2$ ($[M+H]^+$): calcd: 1776.8624, found: 1776.8665.

Conversion of **4** to **3**

15 mg (8.45 μmol) of 4 was dissolved in 5 mL of CH_2Cl_2, to this was added 3.5 mg (84.5 μmol) $NaBH_4$ followed by addition of **3** mL of MeOH. The reaction mixture was stirred under nitrogen atmosphere for 30-40 min. Extraction of the reaction mixture from dichloromethane and subsequent evaporation of the solvent followed by recrystallization from CH_2Cl_2/hexane gave 3 (14.5 mg, quantitative).

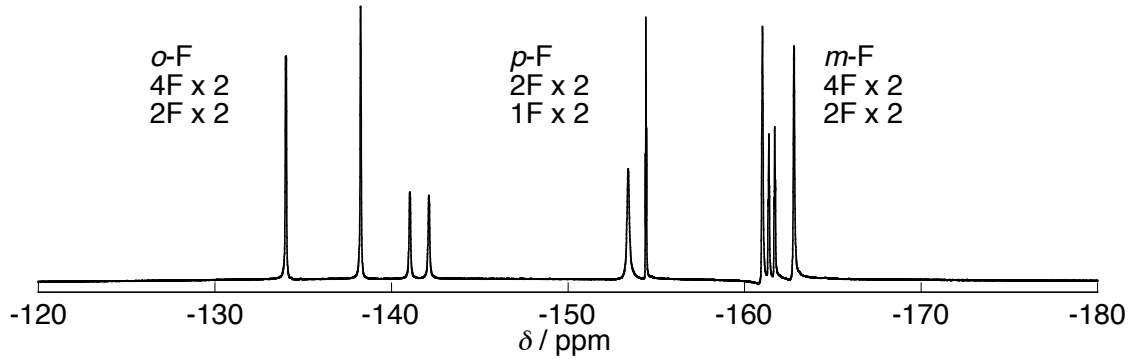


Figure S1. ^{19}F NMR spectrum of **3** in CD_2Cl_2.

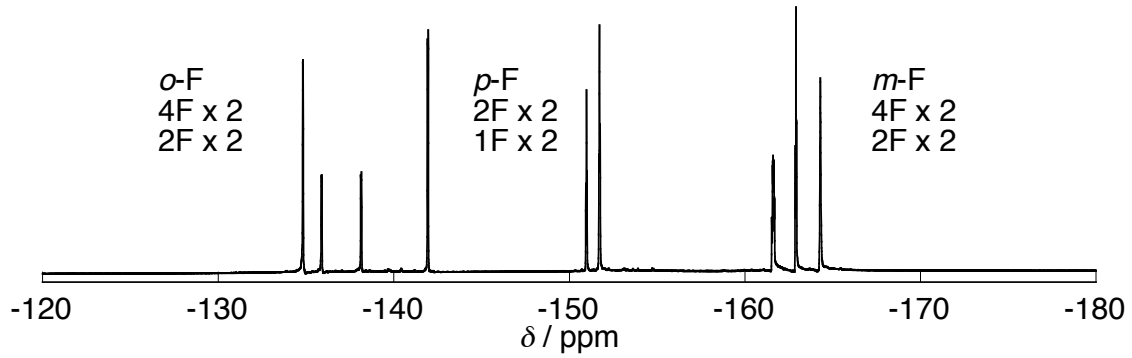


Figure S2. ^{19}F NMR spectrum of **4** in $CDCl_3$.

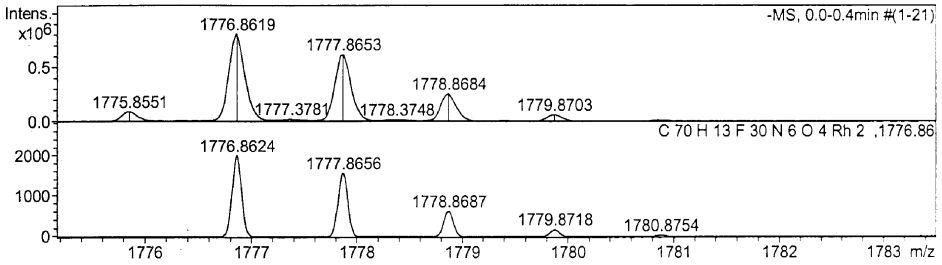


Figure S3. ESI-TOF mass spectrum of **3**.

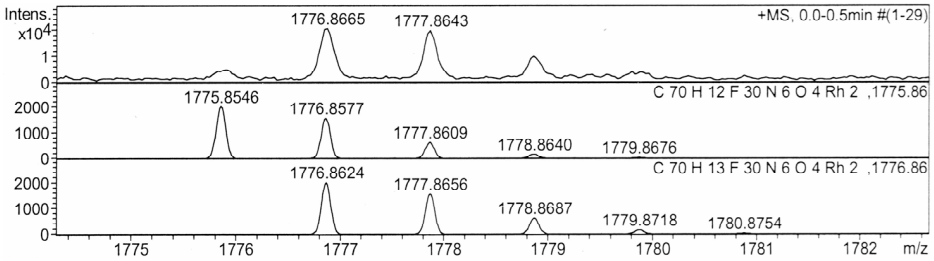


Figure S4. ESI-TOF mass spectrum of **4**.

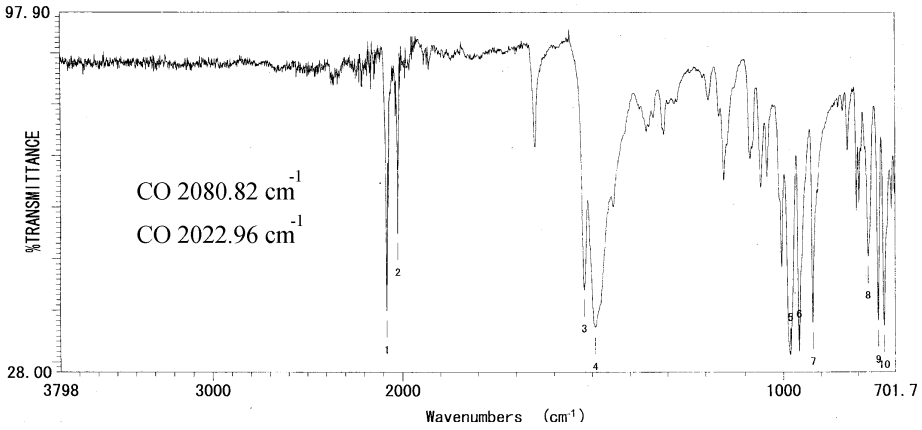


Figure S5. IR spectrum of **4**.

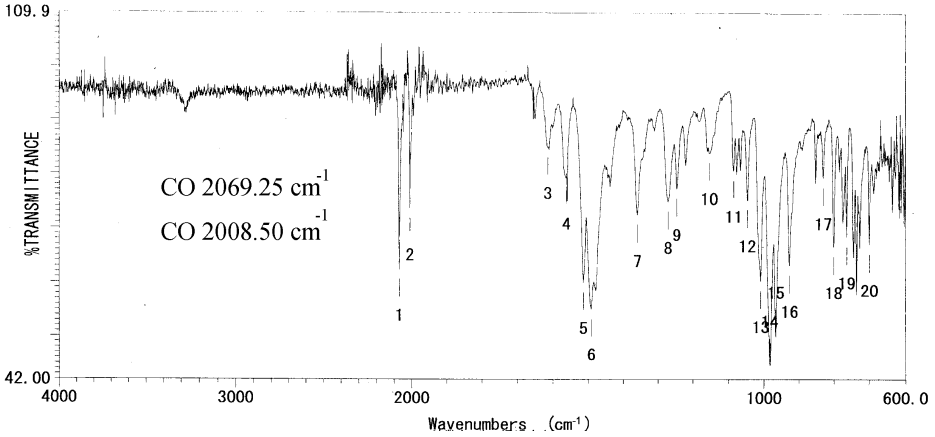


Figure S6. IR spectrum of **3**.

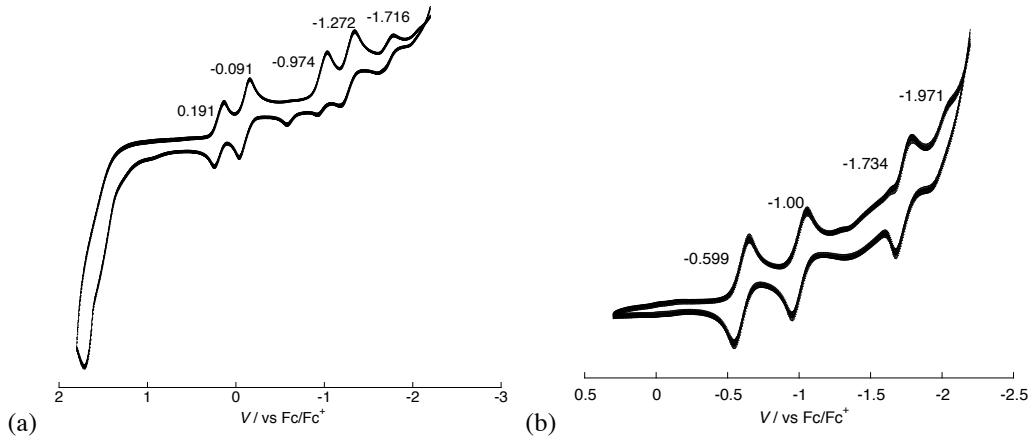


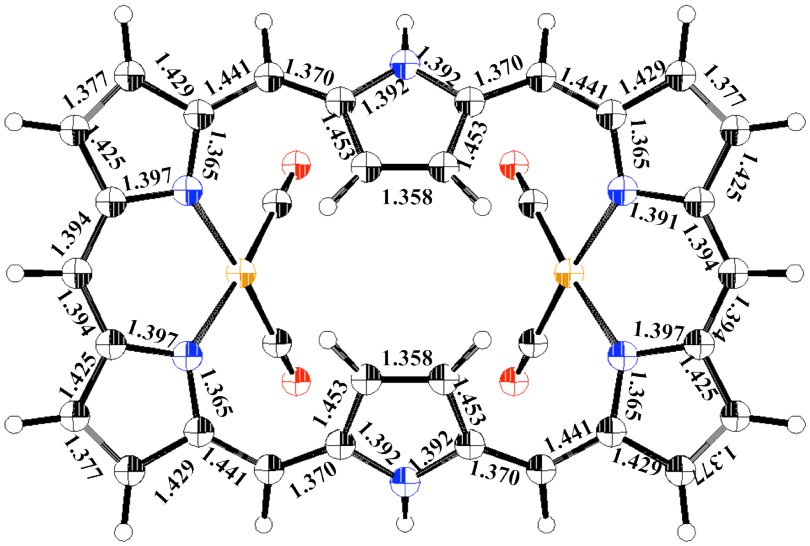
Figure S7. CV of (a) **3**. and (b) **4**.

Table S1. Crystal data and structure refinement for **3** and **4**.

	3	**4**
Formula	$(C_{70}H_{14}F_{30}N_6O_4Rh_2)_2(C_8H_{18})_{1.59}(C_7H_8)_{5.81}$	$(C_{70}H_{12}F_{30}N_6O_4Rh_2)_2(C_8H_{18})_2(C_7H_8)_5$
Formula weight	4269.5	4241.46
Cryst. size (mm^3)	0.50 x 0.50 x 0.30	0.45 x 0.30 x 0.15
Temperature (K)	123(2)	90(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Triclinic	Triclinic
Space group	*P*-1	*P*-1
a (Å)	15.218(5)	15.529(2)
b (Å)	17.094(6)	17.342(2)
c (Å)	18.776(6)	17.546(3)
α (°)	80.895(12)	76.745(3)
β (°)	67.008(11)	72.570(2)
γ (°)	72.583(12)	73.247(3)
V ($Å^3$)	4285(2)	4263.7(10)
Z	1	1
D_c (g/cm^3)	1.654	1.655
Abs. coeff. (mm^{-1})	0. 509	0.511
F(000)	2128	2113
Theta (°)	27.5	26.5
Independent refl.	19304 [*R*(int) = 0.0498]	16828 [*R*(int) = 0.0219]
Absorp. correction	Empirical	Empirical
Refinement method	Full-matrix least-squares on F^2	
GOF	1.050	1.129
R_1 [$I > 2\text{sigma}(I)$]	0.0562	0.0593
R_w (all data)	0.1691	0.1599
CCDC number	720404	720405

*Solvent molecules contained in the crystal lattice of **3** were disordered, and one position was assigned to be occupied by (two octanes) or (one octane and two toluenes). Appropriate restrictions (DFIX for octanes and toluenes and SIMU and ISOR for toluene molecules) were necessary to fix them, but no restriction was applied for the mother skeleton.

Theoretically Optimized Structure



X-ray Crystal Structure

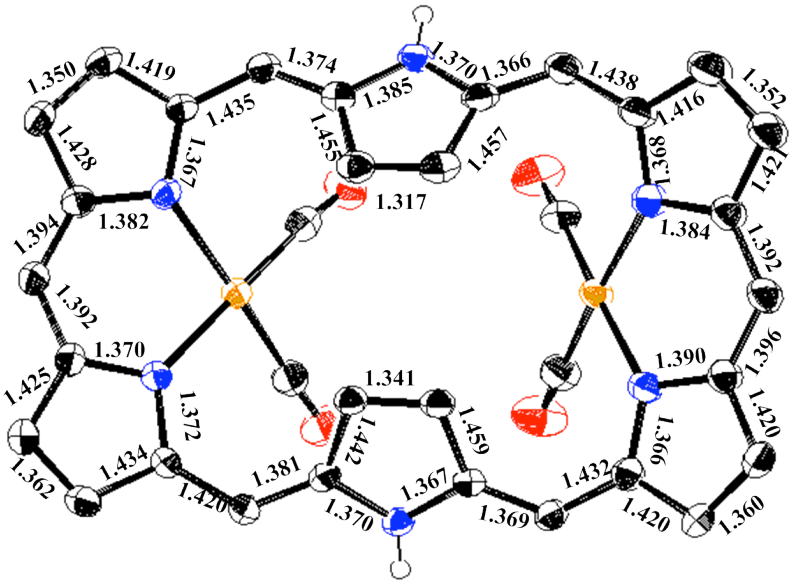


Figure S8. Theoretical and crystal structures of **3**. Pentafluorophenyl substituents were replaced by hydrogen atoms for calculations.

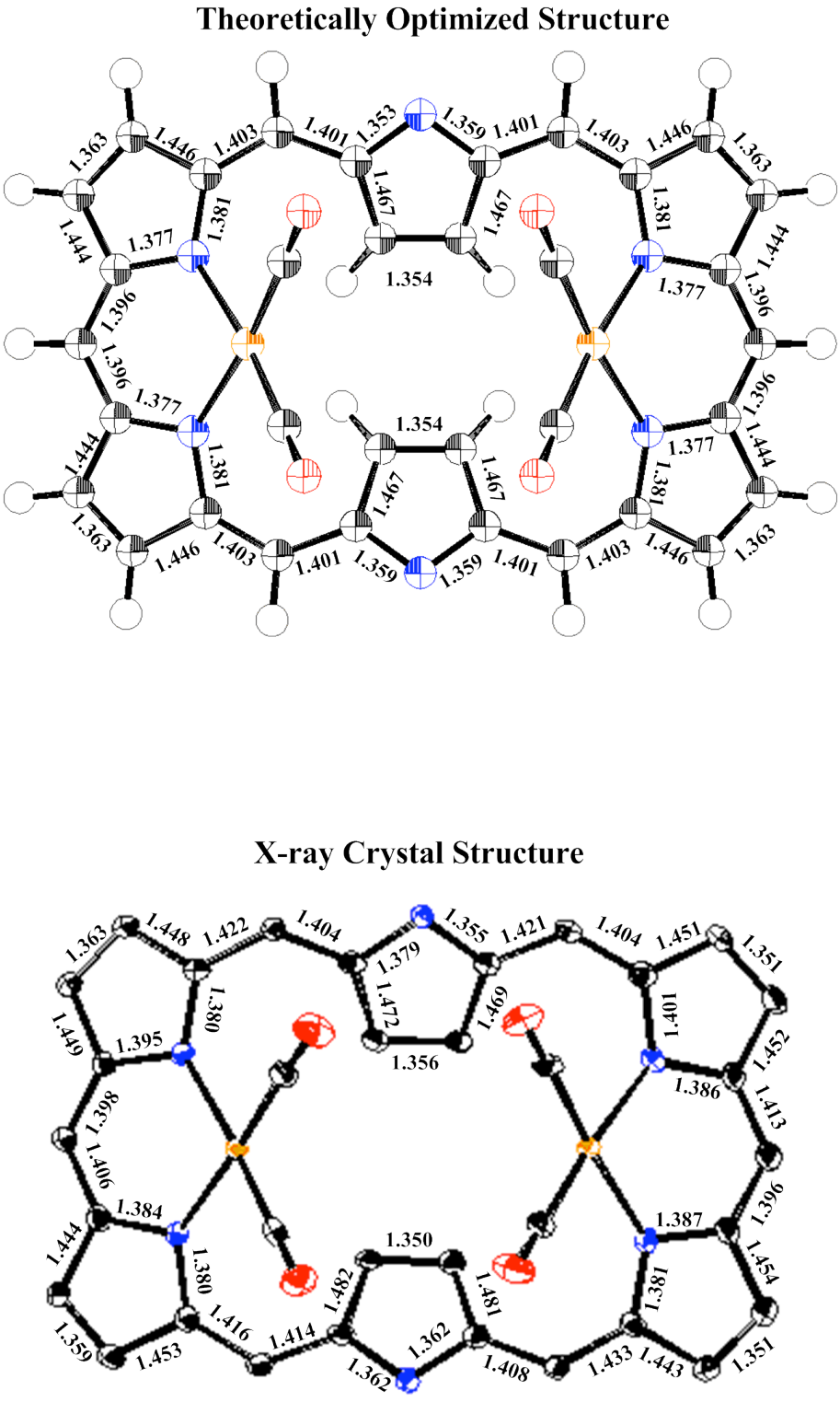


Figure S9. Theoretical and crystal structures of **4**. Pentafluorophenyl substituents were replaced by hydrogen atoms for calculations.

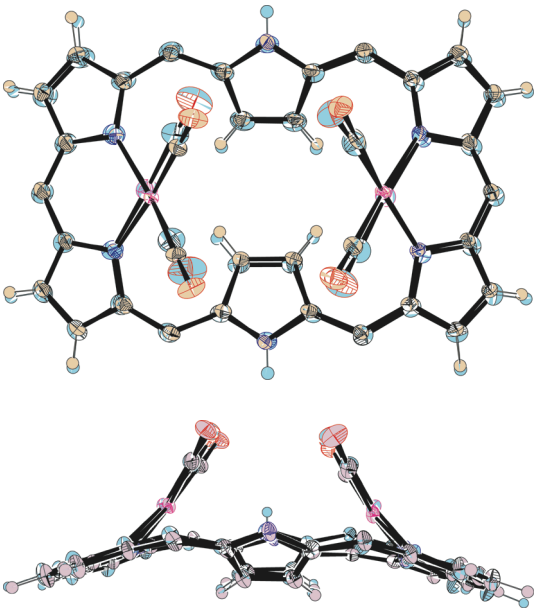


Figure S10. Projection views of **3** (blue) and **4** (orange).

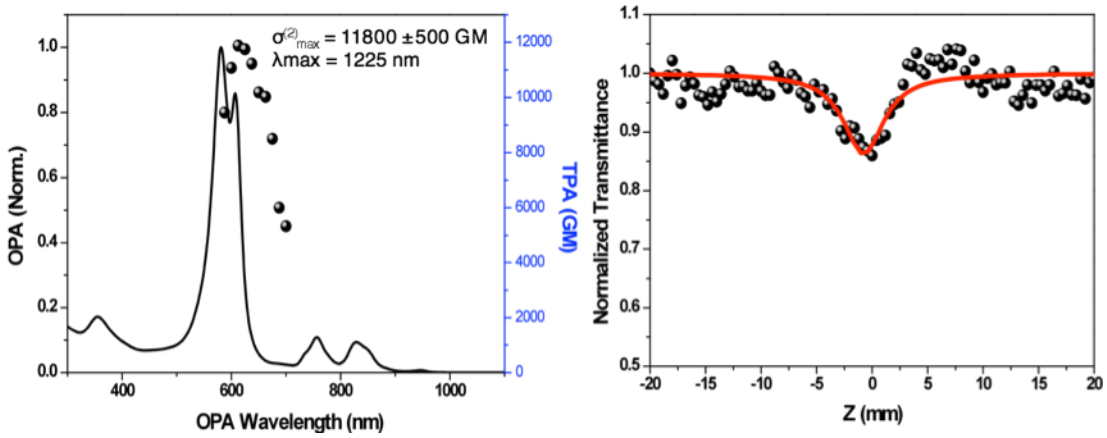


Figure S11. Nonlinear transmittance data and the best fitted curves of **4**.

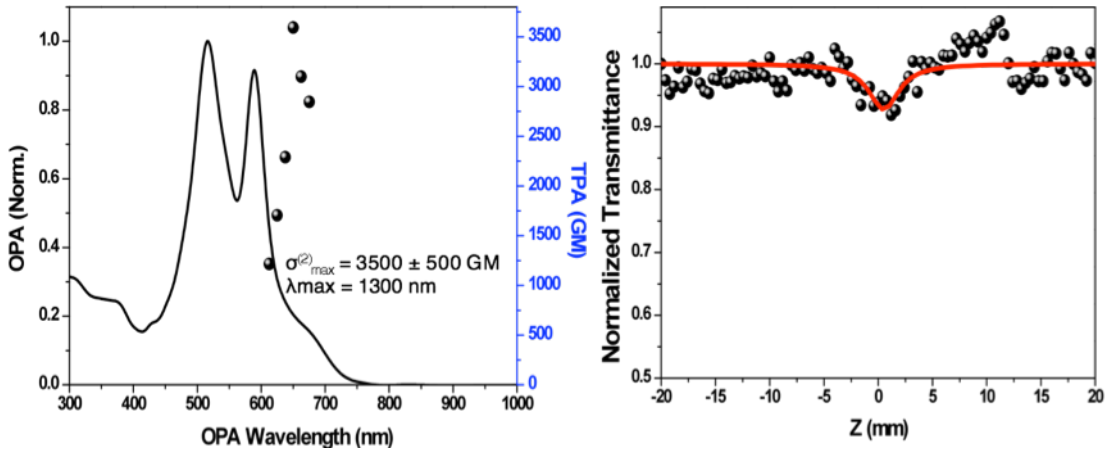


Figure S12. Nonlinear transmittance data and the best fitted curves of **3**.

Sample	Wavelength (nm)	Concentration (mM)	TPA Cross Section (GM)
4	1225	0.10	11800 (±500)
3	1300	0.19	3500 (± 500)