

Supporting Information

Photophysical Properties of Core-modified Expanded Porphyrins: Nature of Aromaticity and Enhancement of Ring-planarity

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Sample Preparation The details of the synthetic procedures and characterizations of five samples are described as follows.

(1) **5,14,23,32-Tetramesityl-37,40,41,44-tetrathia[34]octaphyrin(1.0.1.0.1.0.1.0) 1.** 5,14-Dimesityl-20,21-dithiaterpyrrane (0.25 g, 0.44 mmol), was dissolved in dry CH₂Cl₂ and stirred under nitrogen atmosphere in absence of light for 15 minutes. TFA (0.03 ml, 0.44 mmol) in dry CH₂Cl₂ was added and stirring continued for another one hour. Reaction mixture was opened to air, chloranil (0.1 g, 0.4 mmol) was added refluxed for one hour on a preheated oil bath. The solvent was removed under reduced pressure. The residue obtained was chromatographed on a basic alumina column. A blue color band eluted with petroleum ether: CH₂Cl₂ (7:3) gave a brownish metallic solid identified as tetrathiaoctaphyrin (yield: 0.05 g). Recrystallization from CH₂Cl₂/*n*-hexane afforded gold colored crystals. Decomposes above 225°C. ¹H NMR 300 MHz: (d₈-toluene, 248K): 11.43 (d, J = 3Hz, 2H), 10.95 (d, J = 3Hz, 2H), 10.53(d, J = 6Hz, 2H), 10.46(d, J = 6Hz, 2H), 10.17(br, 4H) 7.76(s, 4H), 7.65(s, 4H), 2.89(s, 6H), 2.84(s, 6H), 2.77(s, 12H), 2.74(s, 12H), -2.28(brs, 2NH), -5.3(d, J = 3Hz, 2H), -5.89(d, J = 3Hz, 2H). FAB MS: 1111(60%) [M+1]. Uv-Vis (CH₂Cl₂) λ_{max} (nm) (ε x 10⁻⁴M⁻¹cm⁻¹): 598 (8.95), 7.54(0.9), 835(4.1), 906(0.7). (CH₂Cl₂ / TFA) λ_{max} (nm) (ε x 10⁻⁴ M⁻¹cm⁻¹): 645(28.18), 794(0.47), 873(0.8), 998(3.57).

(2) **5,14,23,32-Tetramesityl-37,40,41,44-tetraselena[34]octaphyrin(1.0.1.0.1.0.1.0) 2.** A similar procedure as mentioned above was followed with 5,14-dimesityl-20,21-diselenaterpyrrane (0.25g, 0.4 mmol), TFA (0.03 ml, 0.4 mmol) and chloranil (0.1 g, 0.4 mmol). On chromatographic separation with basic alumina, a blue colored band eluted with petroleum ether: CH₂Cl₂ (3:2) gave a brownish metallic solid identified as tetraselenaoctaphyrin (yield: 0.025 g). Golden colored crystals of TFA bound complex of 81 was obtained by recrystallizing from CH₂Cl₂/TFA/*n*-hexane. ¹H NMR 400 MHz: (CDCl₃, 298K): 10.42(s, 2H), 9.85(s, 2H), 9.58 – 9.48(br, 4H), 8.77 – 8.72(br, 4H), 7.57(s, 4H), 7.42(s, 4H), 2.75(s, 6H), 2.66(s, 6H), 2.23(s, 12H), 2.08(s, 12H), -2.1(brs, 4H). FAB MS: 1300(30%) [M+2]. Uv-Vis

(CH₂Cl₂) λ_{\max} (nm) ($\epsilon \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$): 646(28), 745(1.3), 818(2.07), 908(3.1). (CH₂Cl₂ / TFA) λ_{\max} (nm) ($\epsilon \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$): 638(21), 862(2.07).

(3) 5,10,19,24-Tetraphenyl-33,35,36,38,39-pentathia[30]heptaphyrin(1.1.0.1.1.0.0) 3. An equimolar solution of terthiophene diol (0.2 g, 0.43 mmol) and dithia-tetrapyrane (0.22 g, 0.43 mmol) were dissolved in dry CH₂Cl₂ and stirred under nitrogen atmosphere protected from light. TFA (0.03 ml, 0.43 mmol) was added, and stirring was continued for further 60 minutes. Chloranil (0.1 g, 0.43 mmol) was added, and the reaction mixture was opened to air and refluxed for further 60 minutes. The solvent was evaporated under reduced pressure and the residue obtained was chromatographed on basic alumina column. A dark blue colored band eluted with dichloromethane gave bronze colored metallic solid. This was recrystallized from dichloromethane and *n*-hexane. Decomposes above 285°C. ¹H NMR (400 MHz, CDCl₃, 298K): δ = 10.87(d, J = 4Hz, 1H), 10.74(d, J = 4Hz, 1H), 10.71(d, J = 4Hz, 1H), 10.49(d, J = 4Hz, 1H), 10.36(d, J = 4Hz, 1H), 9.83(d, J = 4Hz, 1H), 9.75(d, J = 4Hz, 1H), 9.7(d, J = 4Hz, 1H), 8.71(d, J = 4Hz, 1H), 8.61(d, J = 4Hz, 1H), 8.52(d, J = 4Hz, 1H), 8.30(d, J = 4Hz, 1H), 7.86-8.0(m, 15H), 8.35-8.6(m, 5H), -1.12(d, J = 4Hz, 1H), -2.03(d, J = 4Hz, 1H). ¹H NMR (300 MHz, CDCl₃ / TFA, 233K): δ = 12.39(d, J = 4Hz, 1H), 12.22(d, J = 4Hz, 1H), 12.13(s, 1H), 11.76(d, J = 4Hz, 1H), 11.28(d, J = 4Hz, 1H), 11.12(s, 1H), 11.03(d, J = 4Hz, 1H), 10.6(d, J = 4Hz, 1H), 9.7(d, 1H, 8Hz), 9.65(s, 2H), 9.56(d, J = 8Hz, 1H), 9.43(d, J = 8Hz, 1H), 9.04-8.89(m, 6H), 8.44-8.22(m, 13H), -3.83 (d, J = 4Hz, 1H), -4.16(d, J = 4Hz, 1H), -4.88(bris, 2NH). FAB-MS: (m/z) (%) = 895(75)[M⁺]. UV-Vis (CH₂Cl₂) λ_{\max} (nm) ($\epsilon \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$): 567(30.7), 594sh(20.38), 757(2.7), 826(10.42), 945(2), 1090(2.5). (CH₂Cl₂ / TFA) λ_{\max} (nm) ($\epsilon \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$): 598(37.12), 639(15.01), 914(3.27), 1014(12.7)

(4) 5,10,19,24-Tetraphenyl-29,31,32,34-tetrathia[26]rubiyrin(1.1.0.1.1.0) 4. 5,5'-bis(phenylhydroxymethyl)-2,2'-bithiophene (1 g, 2.65 mmol) and pyrrole (0.184 ml, 2.65 mmol) in dry dichloromethane (800 ml) was stirred under nitrogen atmosphere for 15 minute at room temperature. A

freshly distilled solution of $\text{BF}_3 \cdot \text{OEt}_2$ (2.5M, 10 mol %) in dry CH_2Cl_2 was added, and the reaction mixture was stirred for one additional hour under dark conditions. The resulting solution was open to air and chloranil (1 g, 4 mmol) was added and the mixture was heated to reflux in a preheated oil bath at 50°C for 1 hour. After removal of the solvent, the crude product was purified by column chromatography (basic alumina). After an initial brown fraction was eluted with $\text{CH}_2\text{Cl}_2/\text{EtOAc}$ (70/30), the second dark violet fraction was identified as Tetrathiarubyrin. Yield 28%. ^1H NMR (300 MHz, CDCl_3): $\delta = 7.98$ (m, 12H), 8.55 (m, 8H), 9.06 (s, 4H), 10.49-10.50 (d, $J = 3$ Hz, 4H), 11.64-11.66 (d, $J = 6$ Hz, 4H), (m, 8H), 8.02 (m, 12H). ^1H NMR (300 MHz, CDCl_3/TFA): $\delta = 12.15$ (s, 4H), 11.15 (s, 4H), 9.33 (s, 4H), 8.78-8.76 (m, 8H), 8.23-8.14 (m, 8H). EI-MS: m/z : 1003 (70%) $[(M+2)^+]$.

(5) 5,10,19,24-Tetraphenyl-29,31,32,34-tetraselena[26]rubyrin(1.1.0.1.1.0) 5. 5,5'-bis(phenylhydroxymethyl)-2, 2'-biselenophene (1 g, 2.12 mmol) and pyrrole (0.15 ml, 2.12 mmol) in dry dichloromethane (800 ml) was stirred under nitrogen atmosphere for 15 min at room temperature. Trifluoroacetic acid (0.16 ml, 2.12 mmol) was added to the above mixture. The solution was stirred for further 1 hour under dark conditions. The resulting solution was open to air and chloranil (0.781 g, 3.18 mmol) was added and the mixture was heated to reflux in a preheated oil bath at 50°C for 1 hour. After removal of the solvent, the crude product was purified by column chromatography (basic alumina). A violet band eluted with $\text{CH}_2\text{Cl}_2 : \text{EtOAc}$ (95 : 5) gave green lustrous solid identified as Tetraselenarubyrin. Yield 0.250g, 24%. ^1H NMR (300 MHz, CDCl_3): $\delta = 12.15$ (d, $J = 6$ Hz, 4H), 11.03 (d, $J = 6$ Hz, 4H), 9.31 (s, 4H), 8.61 (m, 8H), 8.02 (m, 12H). ^1H NMR (300 MHz, CDCl_3/TFA): $\delta = 12.15$ (s, 4H), 11.15 (s, 4H), 9.33 (s, 4H), 8.78-8.76 (m, 8H), 8.23-8.14 (m, 8H). EI-MS: m/z : 1003 (70%) $[(M+2)^+]$. $\text{C}_{52}\text{H}_{32}\text{N}_2\text{Se}_4$: C 62.41; H 3.22; N 2.80, found C 62.18; H 3.14; N 2.96.

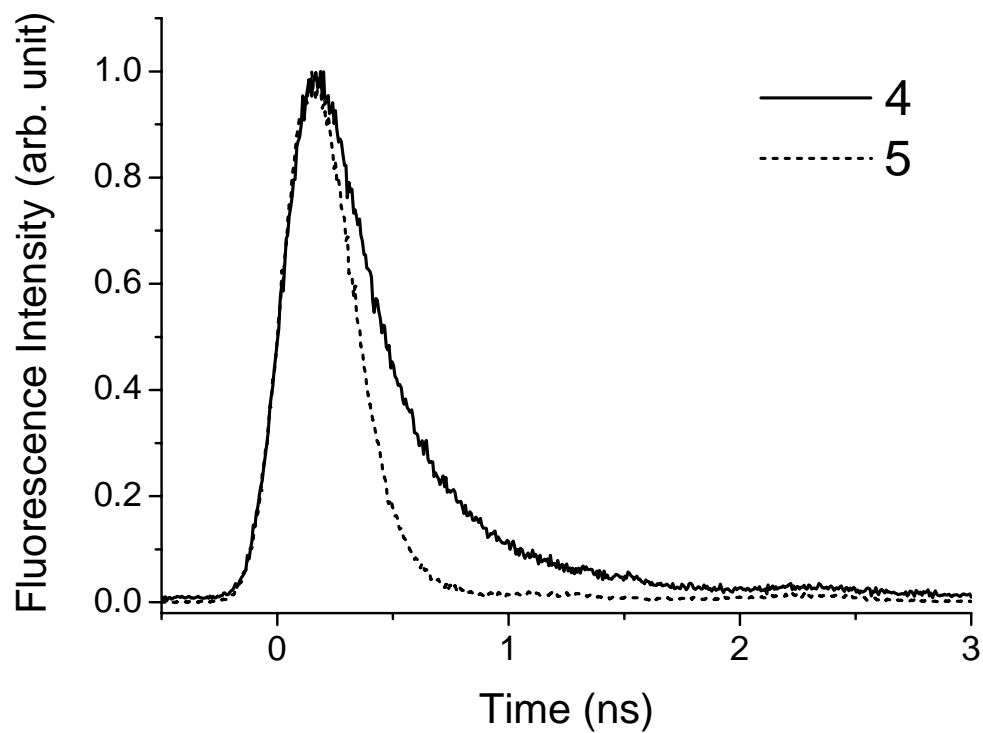


Figure S1. Time-resolved fluorescence decay profiles of **4** and **5** in toluene. The excitation wavelength was 422 nm produced by second-harmonic generation of Ti:sapphire oscillator and fluorescence was monitored at 960 to 970 nm for **4** and **5**, respectively.

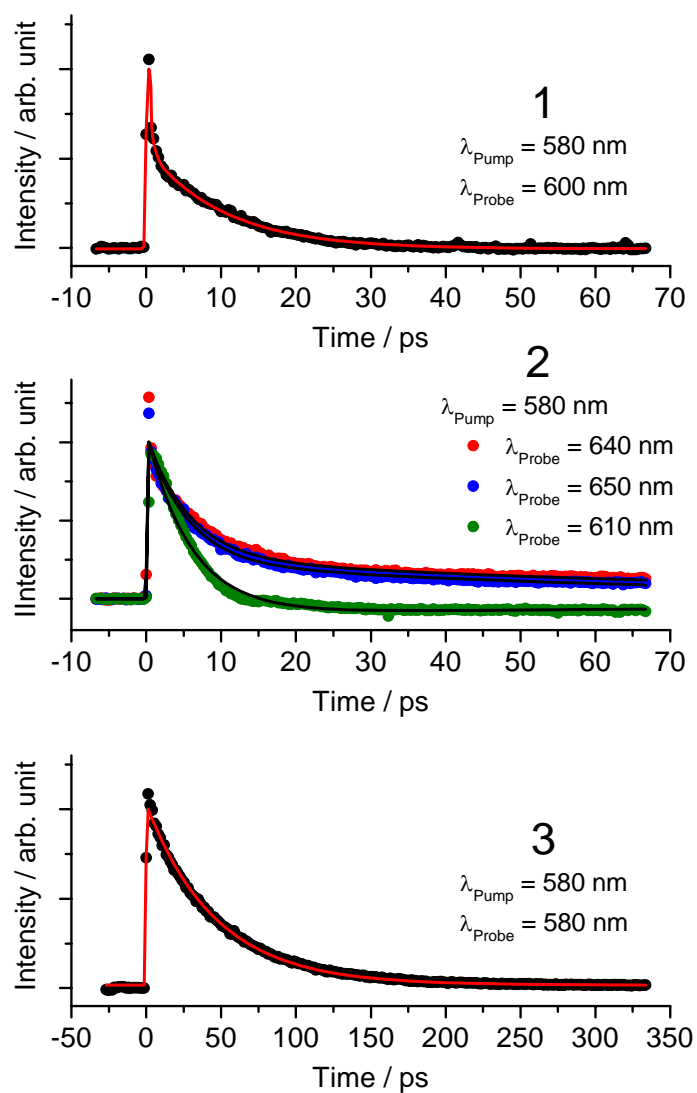


Figure S2. Femtosecond transient absorption decay profiles of **1-3** in toluene with photoexcitation at 580 nm. The singlet state lifetimes of **1**, **2** and **3** were measured at 600, 610 and 580 nm, respectively, which correspond to the B-like band excitation and the ground state bleaching recovery signals.

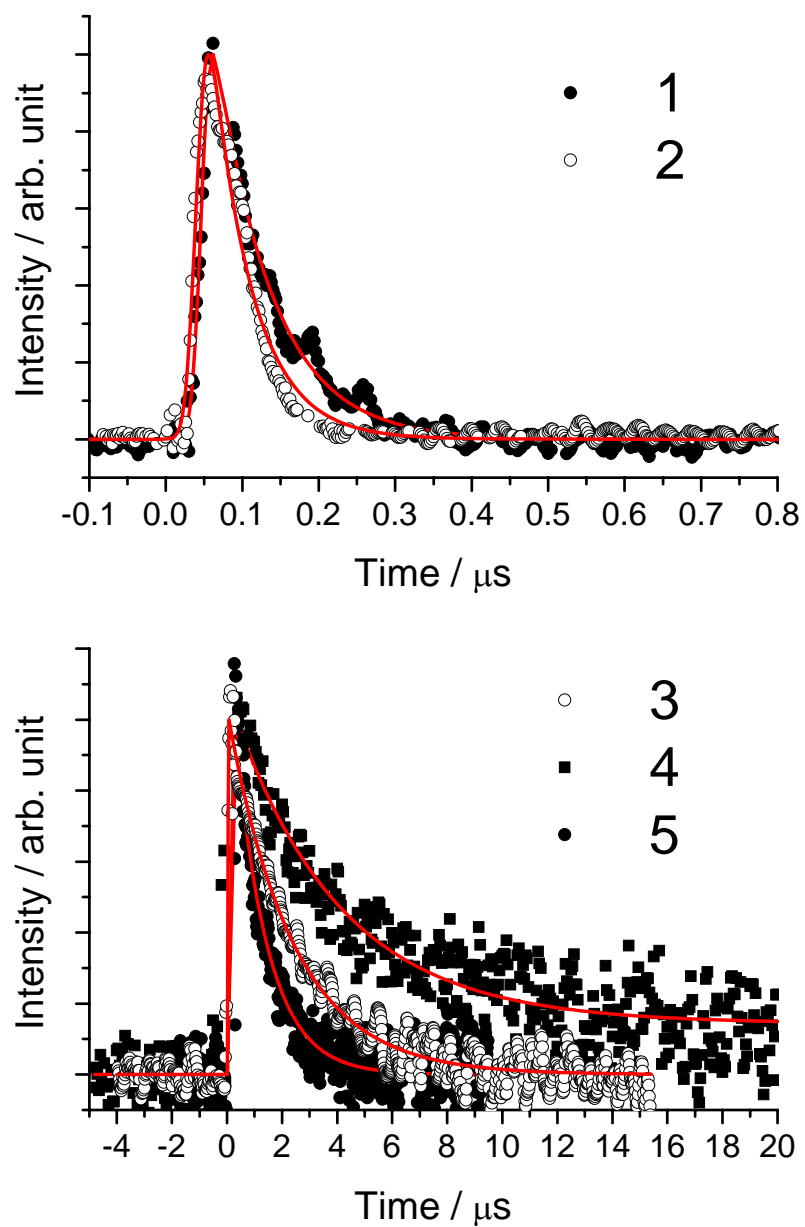


Figure S3. Nanosecond transient absorption decay profiles of **1-5** in toluene. The pump and probe wavelengths are at 610 and 500 nm for **1**, and 650 and 690 nm for **2**, 520 and 790 nm for **3**, 530 and 500 nm for **4**, 550 and 500 nm for **5**, respectively.

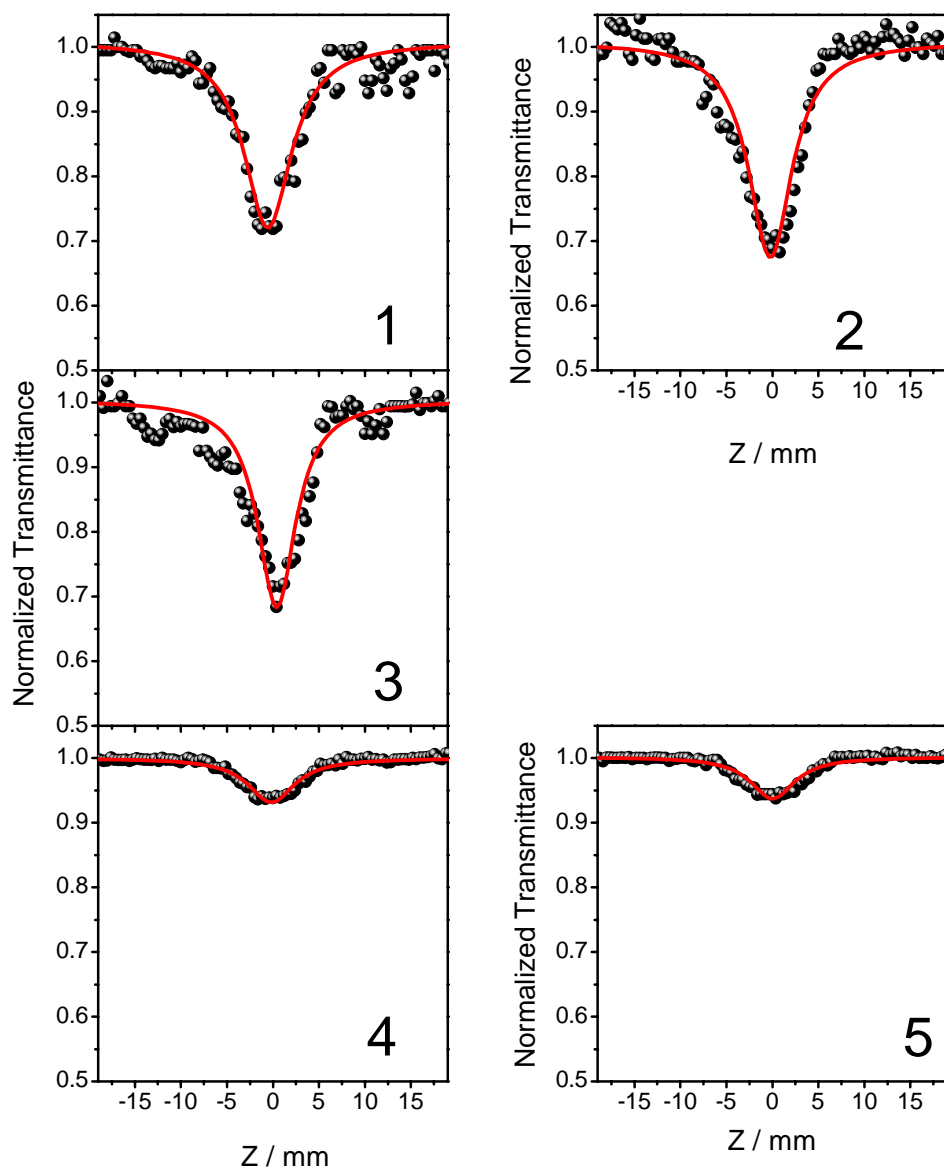


Figure S4. Open-aperture femtosecond Z-scan traces of **1-5** in toluene. Excitation wavelengths are listed in Table 1. The sample concentrations are 0.25 mM. The peak irradiance at the focal point is 80 GW/cm². The solid red lines are the best-fitted curves for the experimental data.