

Supporting Information

Meso – meso linked core modified 22π Smaragdyrins with unusual absorption properties

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General Procedure. All NMR solvents were used as received. Solvents like dichloromethane, tetrahydrofuran and n-hexane were purified and distilled by standard procedure. Electronic spectra were recorded on Perkin-Elmer Lambda 20 UV/Vis spectrophotometer. Proton NMR spectra were obtained on a 400 MHz JEOL spectrometer in CDCl_3 . FAB-MS spectra were obtained on a JEOL-SX-120/DA6000 spectrometer.

5, 10 – dimesityl – 25 – oxasmaragdyrin (1a):

The oxatripyrrane (0.642 g, 1.38 mmol) and dipyrromethane, (0.199 g, 1.38 mmol) were dissolved in dry dichloromethane (400 ml) and stirred under nitrogen atmosphere for 5 min. TFA (0.010 ml, 0.138 mmol) was added and the stirring was continued for 90 min. Chloranil (1.01 g, 4.14 mmol) was added and the reaction mixture was exposed to air and refluxed for a further 90 min. The solvent was evaporated in vacuum. The residue was purified by chromatography on a basic alumina column, second green band which eluted with dichloromethane/petroleum ether (1:1) gave **1a** in (0.20 g, 24%). ^1H NMR (CDCl_3 , 300 MHz, 25°C): δ = 9.83 (s, 1H), 9.40 (d, J = 4.4 Hz, 2H), 9.33 (d, J = 4.0 Hz, 2H), 9,13 (d, J = 4.4 Hz, 2H), 8.54 (s, 2H), 8.31 (d, J = 4.0 Hz, 2H), 7.26 (s, 4H), 2.58 (s, 6H),

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1.83 (s, 12 H); UV/Vis (CH₂Cl₂): λ_{\max} ($\epsilon \times 10^{-4} \text{ M}^{-1} \text{ cm}^{-1}$); 440 (16.3), 471 (4.1), 547 (.42), 590 (.42), 630 (.51), 696 (1.2); FAB-MS: m/z (%): 600 (100) [M⁺]; elemental analysis: calcd (%) for C₄₁H₃₆N₄O: C 81.97, H 6.04, N 9.32; found C 81.96, H 6.03, N 9.33.

5, 10 – (4-tert-butylphenyl) –25 – oxasmaragdyrin 1b

¹H NMR (CDCl₃, 300 MHz, 25°C): δ = 9.92 (s, 1H), 9.49 (d, J = 4.4 Hz, 2H), 9.42 (d, J = 4.0 Hz, 2H), 9.20 (d, J = 4.4 Hz, 2H), 8.84 (s, 2H), 8.52 (d, J = 4.0 Hz, 2H), 8.14 (d, J = 7.2, 4H), 7.80 (d, J = 7.2 Hz, 4H), 1.62 (s, 18H); UV/Vis (CH₂Cl₂): λ_{\max} ($\epsilon \times 10^{-4} \text{ M}^{-1} \text{ cm}^{-1}$); 438 (14.03), 451 (9.34), 545 (0.95), 587 (0.75), 629 (0.74), 693 (0.88); (CH₂Cl₂/TFA): λ_{\max} ($\epsilon \times 10^{-4} \text{ M}^{-1} \text{ cm}^{-1}$); 443 (13.90), 473 (8.33), 594 (0.84), 649 (1.35), 698 (2.11); FAB-MS: m/z (%): 628 (100) [M⁺]; elemental analysis: calcd (%) for C₄₃H₄₀N₄O: C 82.13, H 6.41, N 8.90; found C 82.14, H 6.38, N 8.91.

5, 10 – (4-methylphenyl) –25 – oxasmaragdyrin 1c

¹H NMR (CDCl₃, 300 MHz, 25°C): δ = 9.83 (s, 1H), 9.42 (d, J = 4.4 Hz, 2H), 9.34 (d, J = 4.0 Hz, 2H), 9.13 (d, J = 4.4 Hz, 2H), 8.73 (s, 2H), 8.41 (d, J = 4.0 Hz, 2H), 8.01 (d, J = 7.2, 4H), 7.54 (d, J = 7.2 Hz, 4H), 2.65 (s, 6H); UV/Vis (CH₂Cl₂): λ_{\max} ($\epsilon \times 10^{-4} \text{ M}^{-1} \text{ cm}^{-1}$); 438 (5.78), 452 (3.61), 545 (0.33), 584 (0.21), 626 (0.20), 690 (0.23); (CH₂Cl₂/TFA): λ_{\max} ($\epsilon \times 10^{-4} \text{ M}^{-1} \text{ cm}^{-1}$); 443 (5.74), 473 (2.92), 594 (0.27), 649 (0.50), 700 (0.81); FAB-MS: m/z (%): 544 (100) [M⁺]; elemental analysis: calcd (%) for C₃₇H₂₈N₄O: C 81.59, H 5.18, N 10.28; found C 81.57, H 5.19, N 10.30.

AgPF₆ Promoted dimerization of smaragdyrins:

Meso-meso linked smaragdyrin dimer (2a):

A solution of monomer **1a** (370 mg, 0.614 mmol) in CHCl₃ was shielded from light and cooled to 0°C. A solution of AgPF₆ (5.3 ml, 0.12 M solution in acetonitrile) was added and the mixture was stirred. After 4h, the reaction was stopped. The solvent was evaporated in vacuum, the residue was purified by chromatography on a basic alumina column, second greenish-brown band which eluted with dichloromethane gave dimer **2a** as a green solid (143 mg, 19.3%); ¹H NMR (300 MHz, CDCl₃) δ 9.58 (d, J = 4.2 Hz, 4H), 9.34 (d, J = 4.5 Hz, 4H), 8.73 (s, 4H), 8.59 (d, J = 4.2 Hz, 4H), 8.51 (d, J = 4.2 Hz, 4H), 7.28 (s, 8H), 2.6 (s, 12H), 1.92 (s, 24H), -3.15 (brs, NH); UV / Vis (in CH₂Cl₂): λ_{max} [nm] (ε x 10⁻⁴ M⁻¹cm⁻¹) = 463 (22.11), 559 (2.98), 603 (2.22), 641 (1.84), 723 (2.62); (CH₂Cl₂/TFA(monoproto)): λ_{max}(ε x 10⁻⁴ M⁻¹ cm⁻¹); 465 (19.32), 608 (1.67), 655 (1.64), 732 (2.81); (CH₂Cl₂/TFA(diproto)): λ_{max}(ε x 10⁻⁴M⁻¹cm⁻¹); 470 (18.11), 654 (1.9), 739 (3.95), 849 (3.91): FAB-MS m/z (%) = 1201(90) [(M+2)⁺]; elemental analysis: calcd (%) for C₈₂H₇₀N₈O₂ : C 82.10, H 5.88, N 9.34; found C 82.08, H 5.86, N 9.36

Meso-meso linked smaragdyrin dimer (2b)

A solution of monomer **1b** (200 mg, 0.322 mmol) in CHCl₃ was shielded from light and cooled to 0°C. A solution of AgPF₆ (2.6 ml, 0.12 M solution in acetonitrile) was added and the mixture was stirred. After 4h, the reaction was stopped. The solvent was evaporated in vacuum, the residue was purified by chromatography on a basic alumina

column, second greenish-brown band which eluted with dichloromethane gave dimer **2b** as a green solid (15 mg, 3.75 %); $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 9.63 (d, $J = 4.2$ Hz, 4H), 9.41 (d, $J = 4.2$ Hz, 4H), 8.95 (s, 4H), 8.67 (d, $J = 4.2$ Hz, 4H), 8.65 (d, $J = 4.2$ Hz, 4H), 8.26 (d, $J = 7.8$ Hz, 8H), 7.88 (d, $J = 7.8$ Hz, 8H), 1.21 (s, 36 H); UV / Vis (in CH_2Cl_2): λ_{max} [nm] ($\epsilon \times 10^{-4} \text{ M}^{-1} \text{ cm}^{-1}$) = 460 (15.18), 558 (2.08), 603 (1.61), 641 (1.41), 724 (1.85); ($\text{CH}_2\text{Cl}_2/\text{TFA}(\text{monoproto})$): λ_{max} ($\epsilon \times 10^{-4} \text{ M}^{-1} \text{ cm}^{-1}$); 464 (11.62), 608 (1.44), 655 (1.46), 744 (2.13); ($\text{CH}_2\text{Cl}_2/\text{TFA}(\text{diproto})$): λ_{max} ($\epsilon \times 10^{-4} \text{ M}^{-1} \text{ cm}^{-1}$); 470 (10.45), 607 (1.30), 655 (1.35), 853 (2.79); *FAB-MS* m/z (%) = 1254 (100) [M^+]; elemental analysis: calcd (%) for $\text{C}_{86}\text{H}_{78}\text{N}_8\text{O}_2$: C 82.26, H 6.26, N 8.92; found C 82.24, H 6.28, N 8.91.

Meso-meso linked smaragdyrin dimer (2c)

A solution of monomer **1c** (150 mg, 0.275 mmol) in CHCl_3 was shielded from light and cooled to 0°C . A solution of AgPF_6 (2.3 ml, 0.12 M solution in acetonitrile) was added and the mixture was stirred. After 4h, the reaction was stopped. The solvent was evaporated in vacuum, the residue was purified by chromatography on a basic alumina column, second greenish-brown band which eluted with dichloromethane gave dimer **2c** as a green solid (26 mg, 8.6 %); $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 9.63 (d, $J = 4.2$ Hz, 4H), 9.40 (d, $J = 4.2$ Hz, 4H), 8.94 (s, 4H), 8.67 (d, $J = 4.2$ Hz, 4H), 8.63 (d, $J = 4.2$ Hz, 4H), 8.21 (d, $J = 7.5$ Hz, 8H), 7.67 (d, $J = 7.8$ Hz, 8H), 2.77 (12 H); UV / Vis (in CH_2Cl_2): λ_{max} [nm] ($\epsilon \times 10^{-4} \text{ M}^{-1} \text{ cm}^{-1}$) = 459 (14.2), 559 (2.21), 615 (1.78), 650 (1.29), 721 (1.73). *FAB-MS* m/z (%) = 1086 (100) [M^+]; elemental analysis: calcd (%) for $\text{C}_{74}\text{H}_{54}\text{N}_8\text{O}_2$: C 81.74, H 5.00, N 10.30; found C 81.75, H 5.01, N 10.29.

Dimer obtained by BuLi reaction (2c)

The Smaragdyrin monomer **1c** (0.05 g, 0.092 mmol) was dissolved in dry 50 ml THF and a solution of 1.6 M butyl lithium (0.2 ml, 0.32 mmol) was added at -70°C under stirring. After complete addition the cold bath was removed and stirring continued for an additional 15 min. Subsequently a solution of DDQ (83mg,0.368mmol) in 5 ml dry THF was added and mixture was stirred for a further 30 min at room temperature. The solvent was removed and the residue was subjected to chromatography on a neutral alumina column. The green band which eluted with petroleum-ether/DCM (1:1) gave the tolyl dimer in 30 % yield (29.6 mg).

General method for preparation of monoprotonated and diprotonated smaragdyrin dimer:

7.7×10^{-6} M solution of **2b** in dry dichloromethane was taken in twelve 10 ml volumetric flask. An increasing equivalent of 7.7×10^{-4} M solution of trifluoroacetic acid (TFA) was added to each flask. The remaining volume was made up to the mark by the solvent and shaken well. The electronic absorption spectrum of free base **2b** showed the Soret band at 460 nm. At 0.9 equivalent of TFA, the Soret band was red shifted and observed at 470 nm. Further addition of TFA did not shift the Soret band and termed as diprotonated smaragdyrin dimer. At 0.4 equivalent of TFA, we observed the Soret absorption maxima at 465 nm which was in between the free base **2b** and diprotonated species and considered as monoprotonated state.

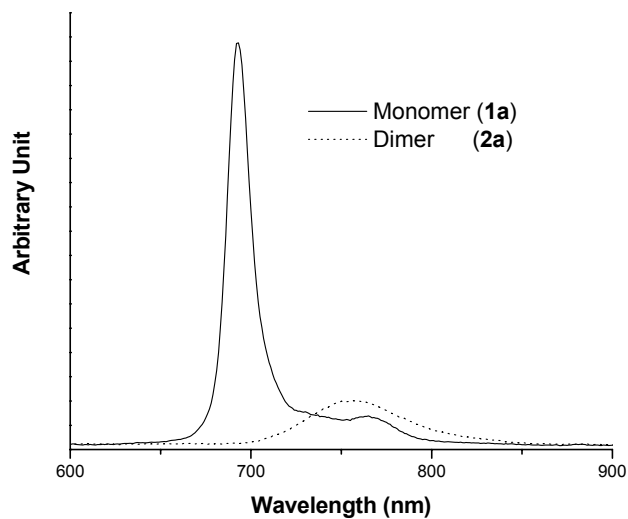


Figure. S1. Fluorescence spectra of **1a** and **2a**.

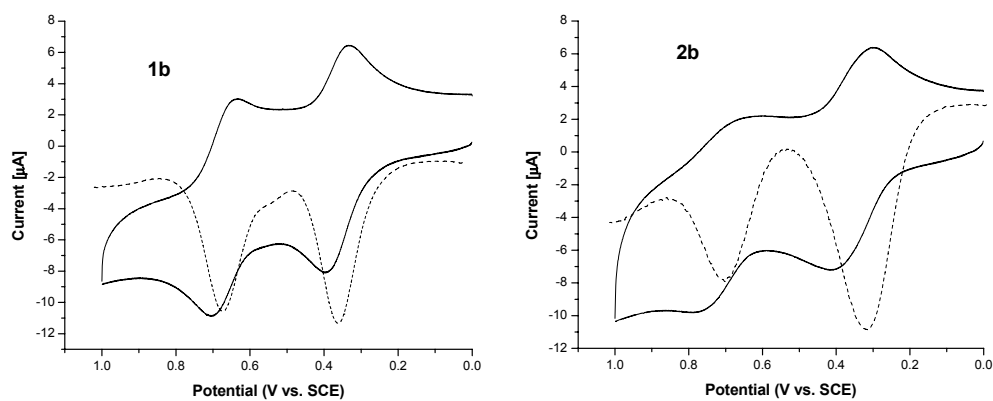


Figure S2. Cyclic voltammograms (—) and differential pulse voltammograms (---) of **1b** and **2b** in CH_2Cl_2 containing 0.1 M TBAPF_6 , recorded at 100 mV/s scan speed.

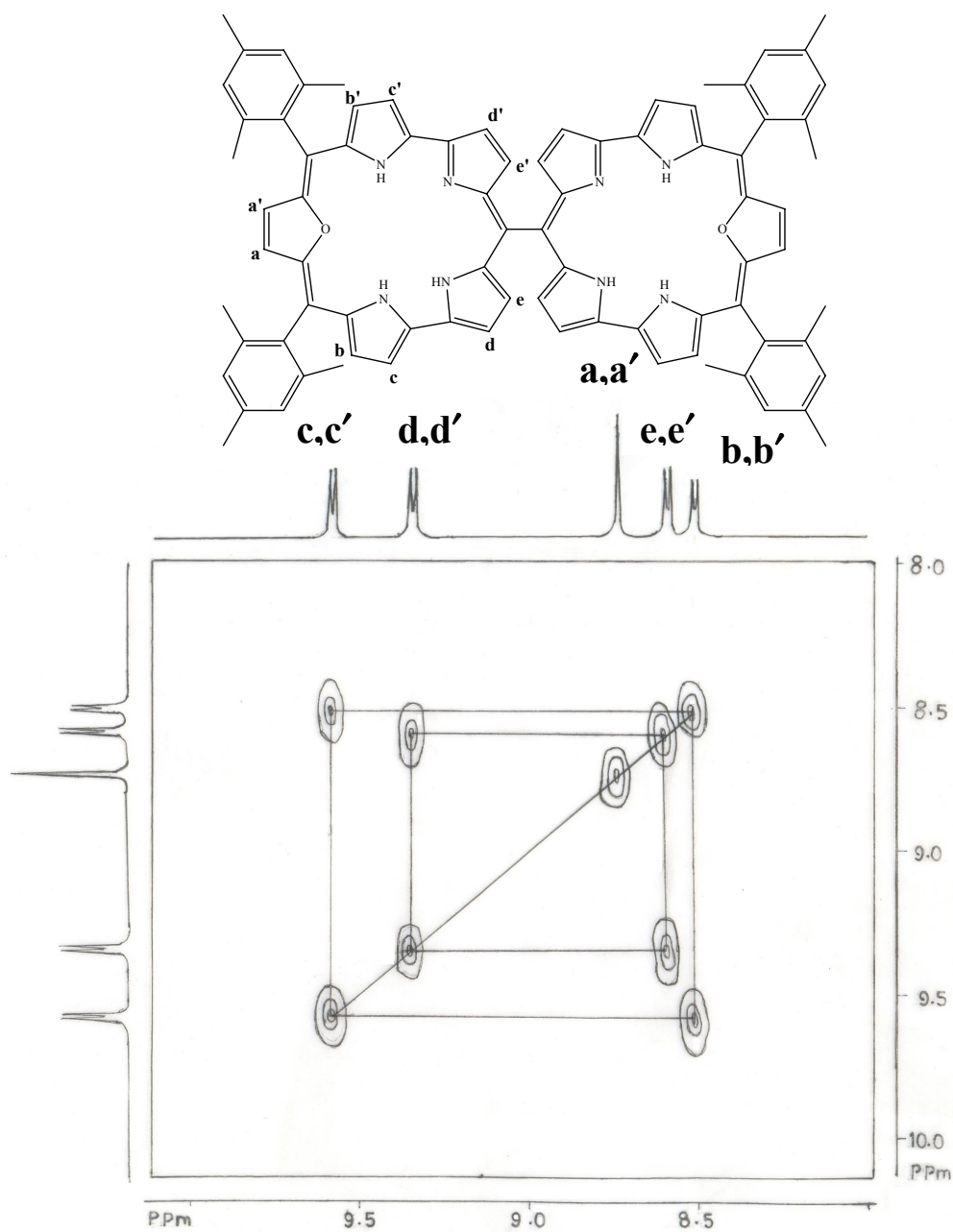


Figure S3. $^1\text{H}/^1\text{H}$ COSY spectrum of **2a** 25° C in CDCl_3 . The observed correlations and assignment are marked.

Calculations on Smaragdyrin Dimer

Methodology

All the molecular systems were studied at BLYP/6-31G* level of density functional theory¹⁻³. All the optimized structures were confirmed as energy minima by normal coordinate analysis. For studying the basic photochemical properties, the widely used time-dependent DFT (TDDFT)⁴⁻⁶ method is employed at BLYP/6-31G* level. All the calculations were carried out with Gaussian03 suit of programs.⁷

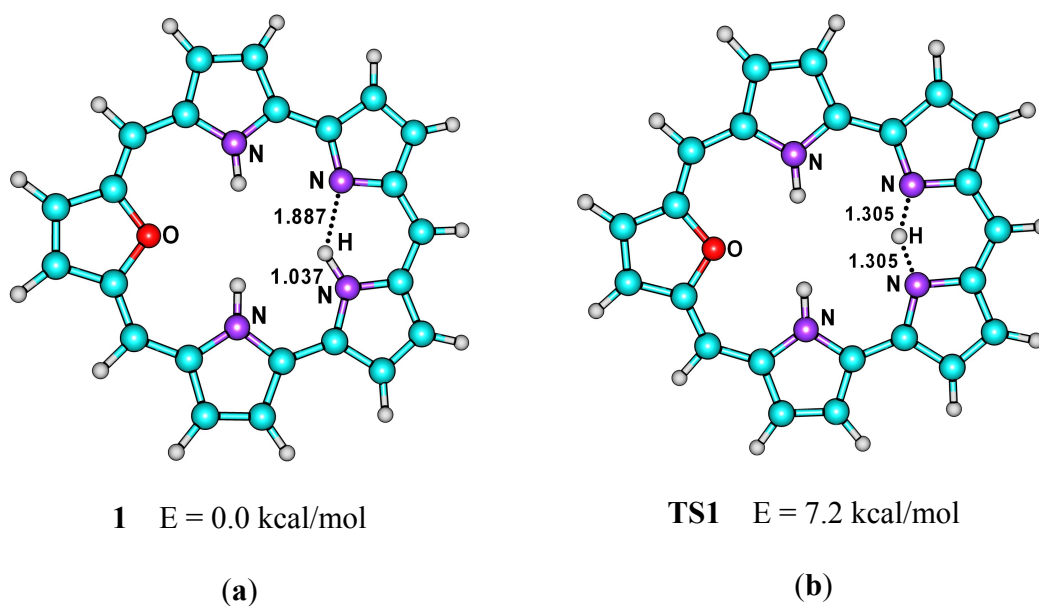


Figure S4. Optimized geometries of (a) smaragdyrin monomer and (b) a transition state for the intramolecular H migration. The relative energy E is also depicted.

Optimized geometry and calculated absorption spectra for **2'**

We have optimized **2'** (smaragdyrin dimer) so that the migrating H atom is equidistant from both the pyrrole nitrogen atoms. In order to simplify the calculations, we have used the N...H distance of 1.305 Å obtained for **TS1** as the value for the N...H distance in **2'**. The structure obtained in this manner (**2'**) is presented in Figure S5. **2'** is found to be 12.6 kcal/mol higher in energy than **2**.

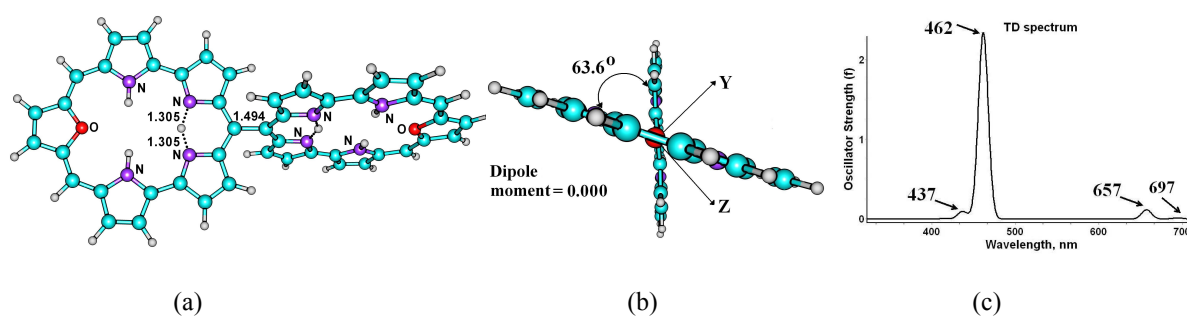


Fig. S5 (a) Optimized geometry of smaragdyrin dimer **2'**. (b) View of **2'** through X-axis direction. (c) Absorption spectra calculated for **2'** at BLYP level.

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