Supporting information

22π Smaragdyrin Molecular Conjugates with Aromatic Phenylacetylenes and Ferrocenes; Syntheses, Electrochemical and Photonic Properties

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1. Synthetic procedure.

General. All NMR solvents were used as received. Solvents like dichloromethane, tetrahydrofuran and n-Hexane were purified and distilled by standard procedures. Tetra-n-butylammoniumhexafluorophosphate from Fluka was used as the supporting electrolyte for cyclic volatammetric studies. 2,5-bis(mesityl hydroxy methyl)furan and 16-oxatripyrrane **3** were prepared according to the published procedure[1] and stored under inert atmosphere at -10 °C. The following compounds were prepared as described in the literature: aldehyde **1c – 1f**,[2] **1h** and **1j**,[3] dipyrromethanes **2a** – **2b**,[4] **2c – 2f**,[2] **2g**,[5] **2h** and **2j**[6], Smaragdyrins **4g** and **5g**[5] were prepared as described in literature. Electronic spectra were recorded on a 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. The Fluorescence spectra were recorded on a SPEX-Fluorolog F112X spectrofluorimeter.

Syntheses

3 – (Ferrocenylacetylenyl)benzaldehyde (1i) : A mixture of **6** (600 mg, 2.58 mmol), 3-iodobenzaldehyde (543 mg, 2.58 mmol), CuI (20 mg, 129 μmol), PPh_3 (33 mg, 129 μmol) and $Pd(PPh_3)_2Cl_2$ (217 mg, 310 μmol) were reacted in the presence of THF(20 ml) and DIEA (7 ml) at room temprature for 48 h on a schlenk line. The mixture was evaporated and the resulting orange solid was chromatographed (silica, CH2Cl2/Hexane 1:1). The second orange band comprised the tittle compound (730 mg, 89 %). ^{1}H NMR ($CDCl_3$, 400 MHz, 25°C): δ = 4.19 (s, 5H), 4.20 (t, 2H, J = 1.6 Hz), 4.45 (t, 2H, J = 1.6 Hz), 7.4 (t, 1H, J = 7.6 Hz), 7.65 (dt, 1H, J = 1.6 Hz), 7.74 (dt, 1H, J = 1.2 Hz), 7.91 (m,

1H), 9.94 (s, 1H); FAB-MS: m/z (%): 314 (100) [M^+]**;** elemental analysis: calcd (%) for $C_{19}H_{14}FeO$: C 72.63, H 4.49; found: C 72.64 H 4.51.

3 – (Ferrocenylphenylacetylenyl)benzaldehyde (1k) : The above procedure was used by using **7** and 3-iodobenzaldehyde to obtain the aldehyde **1k**. ^{1}H NMR ($CDCl_3$, 400 MHz, 25°C): δ = 4.01 (s, 5H), 4.29 (t, 2H, J =1.6 Hz), 4.6 (t, 2H, J = 1.6Hz), 7.39 – 7.47 (m, 5H), 7.70 – 7.78 (m, 2H), 7.96 (s, 1H), 9.96 (s, 1H); FAB-MS: m/z (%): 390 (100) [M^+]**;** elemental analysis: calcd (%) for $C_{25}H_{18}FeO$: C 76.94, H 4.64; found: C 76.92, H 4.64.

5 – (3 – Ferrocenylacetylenylphenyl)dipyrromethane (2i): A mixture of Pyrrole (6 ml, 89 mmol) and **1i** (0.7 g, 2.22 mmol) was degassed with stream of argon. Then trifluoroacetic acid (17 μl) was added and the mixture was stirred under argon at room temprature for 10 min and then quenched with 0.1 M NaOH. The organic pahse was washed with water dried over anhydrous sodium sulfate and concentrated to afford an orange oil. The oil was purified by column chromatography (silica, CH_2Cl_2/Hexane, 1:1) to afford a yellow oil (696 mg, 72 %). ^{1}H NMR ($CDCl_3$, 400 MHz, 25°C): δ = 7.80 (brs, 2H), 7.01 – 7.30 (m, 4H), 6.57 (q, 2H), 6.10 (q, 2H), 5.82 (q, 2H), 5.45 (s, 1H), 4.45 (t, 2 H, J = 1.6 Hz), 4.19 (s, 7H); FAB-MS: m/z (%): 430 (40) [M^+]**;** elemental analysis: calcd (%) for $C_{27}H_{22}N_2Fe$: C 75.35, H 5.15, N 6.50; found: C 75.31, H 5.14, N 6.53.

The above procedure was followed using respective aldehydes to get other dipyrromethanes.

5 – [3 – (Ferrocenylphenylacetylenyl)phenyl)dipyrromethane (2k): ^{1}H NMR ($CDCl_3$, 400 MHz, 25°C): δ = 7.9 (s, 1H), 7.80 (brs, 2H), 7.70 – 7.78 (m, 2H), 7.49 – 7.35 (m, 5H), 6.58 (q, 2H), 6.10 (q, 2H), 5.80 (q, 2H), 5.45 (s, 1H), 4.6 (2H, t, J = 1.6 Hz), 4.2 (s,

7 H); FAB-MS: m/z (%): 506 (15) [M^+]**;** elemental analysis: calcd (%) for $C_{33}H_{26}N_2Fe$: C 78.26, H 5.17, N 5.53; found: C 78.20, H 5.15, N 5.50.

5, 10 – dimesityl –25 – oxasmaragdyrin 4a: The oxatripyrrane **3** (0.642 g, 1.38 mmol) and dipyrromethane 2a (R = H), (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 **4a** in (0.20 g, 24%). ^{1}H NMR ($CDCl_3$, 400 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), 1.83 (s, 12 H); UV/Vis (CH_2Cl_2): λ_{max} (ε x 10^{-4} $M^{-1}cm^{-1}$); 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 $C_{41}H_{36}N_4O$: C 81.97, H 6.04, N 9.32; found C 81.96, H 6.03, N 9.33.

5, 10 – dimesityl – 19 – phenyl – 25 – oxasmaragdyrin 4b: ^{1}H NMR ($CDCl_3$, 400 MHz, 25°C): δ = 9.42 (d, J = 4.5 Hz, 2H), 9.33 (d, J = 4.5 Hz, 2H), 8.91 (d, J = 4.5 Hz, 2H), 8.56 (s, 2H), 8.39 (d, J = 4.5 Hz, 2H), 8.15 (m, 2H), 7.61 – 7.84 (m, 3H), 7.26 (s, 4H), 2.65 (s, 6H), 1.92 (s, 12H); UV/Vis (CH_2Cl_2): λ_{max} (ε x 10^{-4} $M^{-1}cm^{-1}$); 445 (7.7), 554 (.55), 594 (.45), 638 (.43), 701 (.53); FAB-MS: m/z (%): 676 (100) [M^+]**;** elemental analysis: calcd (%) for $C_{47}H_{40}N_4O$: C 83.40, H 5.95, N 8.27; found C 83.42, H 5.90, N 8.30.

5, 10 – dimesityl – 19 – (4 – phenylacetylenylphenyl) – 25 – oxasmaragdyrin (**4c**): ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.40 (d, J = 4.16 Hz, 2H), 9.31 (d, J = 4.4 Hz, 2H), 8.88 (d, J = 4.4 Hz, 2H), 8.52 (s, 2H), 8.32 (d, J = 4.16 Hz, 2H), 8.31 (d, J = 8.08 Hz, 2H), 7.94 (d, J = 8.08 Hz, 2H), 7.62 – 7.65 (m, 2H), 7.35 – 7.39 (m, 3H), 7.26 (s, 4H), 2.58 (s, 6H), 1.85 (s, 12H); UV / Vis (in CH_2Cl_2): λ_{max} [nm] (ε x 10^{-4} $M^{-1}cm^{-1}$) = 455 (27.7), 486 (sh, 8.4), 605 (1.4), 659 (1.9), 729 (4.5); FAB-MS: m/z (%) = 776 (100) [M^+]; elemental analysis: calcd (%) for $C_{55}H_{44}N_4O$: C 85.02, H 5.70, N 7.21. Found: C 85.05, H 5.71, N 7.19.

5, 10 – dimesityl – 19 – (3– phenylacetylenylphenyl) – 25 – oxasmaragdyrin (4d): ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.40 (d, J = 4.16 Hz, 2H), 9.32 (d, J = 4.4 Hz, 2H), 8.87 (d, J = 4.4 Hz, 2H), 8.53 (s, 2H), 8.32 (d, J = 4.16 Hz, 2H), 7.97 (m, 1H), 7.69 (m, 3H), 7.59 (m, 2H), 7.35 (m, 3H), 7.26 (s, 4H), 2.58 (s, 6H), 1.85 (s, 12H); UV / Vis (in CH_2Cl_2): λ_{max} [nm] (ε x 10^{-4} $M^{-1}cm^{-1}$) = 451 (21.65), 483 (sh, 7.8), 607 (1.02), 661 (1.59), 721 (3.5); FAB-MS m/z (%) = 776 (100) [M^+]; elemental analysis: calcd (%) for $C_{55}H_{44}N_4O$: C 85.02, H 5.70, N 7.21. Found: C 85.03, H 5.70, N 7.18.

5, 10 – dimesityl – 19 – [4 – ((phenylacetylenyl) phenylacetylenyl) phenyl] – 25 – oxasmaragdyrin (**4e**): ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.45 (d, J = 4.4 Hz, 2H), 9.39 (d, J = 4.4 Hz, 2H), 8.97 (d, J = 4.4 Hz, 2H), 8.60 (s, 2H), 8.49 (d, J = 4.4 Hz, 2H), 8.39 (d, J = 8.08 Hz, 2H), 8.05 (d, J = 8.08 Hz, 2H), 7.54 (m, 6H), 7.36 (m, 3H), 7.26 (s, 4H), 2.65 (s, 6H), 1.92 (s, 12H); UV/ Vis (in CH_2Cl_2): λ_{max} [nm] (ε x 10^{-4} $M^{-1}cm^{-1}$) = 457 (7.6), 486 (2.75), 614 (0.49), 661 (0.68), 729 (1.5); FAB-MS m/z (%) = 877 (100%) [M^+]; elemental analysis: calcd (%) for $C_{63}H_{48}N_4O$: C 86.27, H 5.51, N 6.38. Found: C 86.25, H 5.52, N 6.36.

5, 10 – dimesityl – 19 – [3– ((phenylacetylenyl) phenylacetylenyl) phenyl] – 25 – oxasmaragdyrin (**4f**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.48 (d, J = 4.4 Hz, 2H), 9.39 (d, J = 4.4 Hz, 2H), 8.96 (d, J = 4.4 Hz, 2H), 8.61 (s, 2H), 8.39 (d, J = 4.4 Hz, 2H), 8.42 (d, J = 8.4 Hz, 2H), 8.03 (d, J = 8.4 Hz, 2H), 7.89 (s, 1H), 7.50-7.54 (m, 4H), 7.35-7.38(m, 4H), 7.26 (s, 4H), 2.65 (s, 6H), 1.92 (s, 12H); UV / Vis (in CH_2Cl_2): λ_{max} [nm] (ε x 10^{-4} $M^{-1}cm^{-1}$) = 451 (28), 556 (1.9), 597 (1.5), 640 (1.2), 705 (2.0); FAB-MS m/z (%) = 877 (100%) [M^+]; elemental analysis: calcd (%) for $C_{63}H_{48}N_4O$: C 86.27, H 5.51, N 6.38. Found C 86.28, H 5.50, N 6.37.

5, 10 – dimesityl – 19 – (4 – ferrocenylacetylenylphenyl) – 25 – oxasmaragdyrin 4h: ^{1}H NMR ($CDCl_3$, 400 MHz, 25°C): δ = 9.46 (d, J = 4.4 Hz, 2H), 9.37 (d, J = 4 Hz, 2H), 8.95 (d, J = 4 Hz, 2H), 8.59 (s, 2H), 8.37 (d, J = 4.4 Hz, 2H), 8.35 (d, J = 8.4 Hz, 2H), 7.97 (d, J = 8.4 Hz, 2H), 7.30 (s, 4H), 4.67 (t, J = 1.6 Hz, 2H), 4.34 (t, J = 1.6 Hz, 2H), 4.04 (s, 5H), 2.65 (s, 6H), 1.92 (s, 12 H); UV/Vis (CH_2Cl_2): λ_{max} (ε x 10^{-4} $M^{-1}cm^{-1}$); 451 (23.2), 556 (1.6), 597 (1.6), 641 (1.4), 707 (1.9); FAB-MS: m/z (%): 886 (100) [$(M+2)^+$]**;** elemental analysis: calcd (%) for $C_{59}H_{48}N_4OFe$: C 80.08, H 5.46, N 6.33; found C 80.07, H 5.48, N 6.31.

5, 10 – dimesityl – 19 – (3 – ferrocenylacetylenylphenyl) – 25 – oxasmaragdyrin 4i: ^{1}H NMR ($CDCl_3$, 400 MHz, 25°C): δ = 9.42 (d, J = 4.4 Hz, 2H), 9.34 (d, J = 4.4 Hz, 2H), 8.93 (d, J = 4.4 Hz, 2H), 8.56 (s, 2H), 8.33 (d, J = 4.4 Hz, 2H), 7.89 (m, 1H), 7.78 (m, 1H), 7.54 (m, 2H), 7.24 (s, 4H), 4.55 (t, J = 1.6 Hz, 2H), 4.25 (s, 7H), 2.63 (s, 6H), 1.96 (s, 12 H); UV/Vis (CH_2Cl_2): λ_{max} (ε x 10^{-4} $M^{-1}cm^{-1}$); 448 (21.3), 483 (7.6), 554 (1.4), 597 (1.4), 644 (1.3), 716 (1.7); FAB-MS: m/z (%): 886 (100) [$(M+2)^+$]**;** elemental analysis: calcd (%) for $C_{59}H_{48}N_4OFe$: C 80.08, H 5.46, N 6.33; found C 80.06, H 5.49, N 6.30.

5, 10 – dimesityl – 19 – [4 –(Ferrocenylphenylacetylenyl)phenyl] – 25 – oxasmaragdyrin 4j: ^{1}H NMR (400 MHz, $CDCl_3$, 25° C): δ = 9.46 (d, J = 4.2Hz, 2H), 9.37 (d, J = 4.3Hz, 2H), 8.97 (d, J = 4.3Hz, 2H), 8.59 (s, 2H), 8.39 (d, J = 4.2Hz, 2H), 8.37 (d, 2H), 8.02 (d, 2H), 7.62 (d, J = 8.1Hz, 2H), 7.50 (d, J = 8.1Hz, 2H), 7.34 (m, 4H), 4.73 (d, 2H), 4.39 (s, 2H), 4.09 (s, 5H), 2.65 (s, 6H), 1.92 (s, 12H); UV/Vis (CH_2Cl_2): λ_{max} (ε x 10^{-4} $M^{-1}cm^{-1}$); 455(23.2), 485 (6.7), 556 (1.6), 601 (1.3), 657 (1.1), 729 (1.8); FAB-MS: m/z (%): 962 (50) [$(M+2)^+$]; elemental analysis: calcd (%) for $C_{65}H_{52}N_4OFe$: C 81.22, H 5.45, N 5.83; found: C 81.28, H 5.51, N 5.87.

5, 10 – dimesityl – 19 – [3 –(Ferrocenylphenylacetylenyl)phenyl] – 25 – oxasmaragdyrin 4k: ^{1}H NMR (400 MHz, $CDCl_3$, 25° C): δ = 9.46 (d, J = 4.4 Hz, 2H), 9.38 (d, J = 4.1 Hz, 2H), 8.95 (d, J = 4.4 Hz, 2H), 8.59 (s, 2H), 8.37 (d, J = 4.1 Hz, 2H), 7.94 (d, 1H), 7.70 – 7.78 (m, 2H), 7.47 – 7.39 (m, 5H), 7.26 (s, 4H), 4.67 (t, J = 1.6 Hz, 2H), 4.34 (t, J = 1.6 Hz, 2H), 4.04 (s, 5H), 2.65 (s, 6H), 2.02 (s, 12H); UV/Vis (CH_2Cl_2): λ_{max} (ε x 10^{-4} $M^{-1}cm^{-1}$); 450 (22.3), 483 (6.7), 554 (1.3), 597 (1.3), 646 (1.1), 720 (1.7); FAB-MS: m/z (%): 962 (60) [$(M+2)^+$]; elemental analysis: calcd (%) for $C_{65}H_{52}N_4OFe$: C 81.22, H 5.45, N 5.83; found: C 81.23, H 5.45, N 5.90.

[5, 10 – dimesityl –25 – oxasmaragdyrin]dicarbonyl rhodium-(I) Salt 5a: Compound **4a** (0.030 g, 0.05 mmol) was dissolved in dry dichloromethane. Anhydrous sodium acetate (0.041 g, 0.50 mmol) was added to the solution followed by di-μ-chlorobis[dicarbonylrhodium(I)] (0.029 g, 0.075 mmol), and the mixture was stirred under reflux for 2 h. The solvent was evaporated and was chromatographed by using silica gel column with dichloromethane solvent. Removal of the solvent gave a purple solid (0.032 g, 86.4 %). ^{1}H NMR ($CDCl_3$, 400 MHz, 25°C): δ = 9.99 (s, 1H), 9.42 (m,

2H), 9.10 (d, J = 4.4 Hz, 2H), 8.97 (d, J = 4.4 Hz, 2H), 8.61 (s, 2H), 8.38 (m, 2H), 7.26 (s, 4H), 2.66 (s, 6H), 1.99 (s, 6H), 1.78 (s, 6H), - 1.61 (s, 2H) ; IR (KBr): ν_{max}/ cm^{-1} = 2007, 2072 (CO); UV/Vis (CH_2Cl_2): λ_{max} (ε x 10^{-4} $M^{-1}cm^{-1}$); 454 (12.3), 474 (7.7), 567 (1.1), 611 (1.2), 631 (1.2), 691 (1.3); FAB-MS: m/z (%): 758 (25) [M^+]**;** elemental analysis: calcd (%) for $C_{43}H_{35}N_4O_3Rh$: C 68.07, H 4.65, N 7.38; found C 68.06, H 4.65, N 7.37.

[5, 10 – dimesityl – 19 – phenyl – 25 – oxasmaragdyrin] dicarbonyl rhodium-(I) 5b : ^1H NMR ($CDCl_3$, 400 MHz, 25°C): δ = 9.46 (m, 2H), 9.13 (d, J = 4.5 Hz, 2H), 8.71 (d, J = 4.5 Hz, , 2H), 8.64 (s, 2H), 8.40 (m, 2H), 8.28 (m, 2H), 7.78 (m, 3H), 7.26 (s, 4H), 2.65 (s, 6H), 1.99 (s, 6H), 1.86 (s, 6H), - 1.47 (s, 2H); IR (KBr): ν_{max}/ cm^{-1} = 2007, 2072 (CO); UV/Vis (CH_2Cl_2): λ_{max} (ε x 10^{-4} $M^{-1}cm^{-1}$); 459 (2.1), 479 (1.59), 570 (.36), 616 (.35), 698 (.33); FAB-MS: m/z (%): 834 (25) [M^+]**;** elemental analysis: calcd (%) for $C_{49}H_{39}N_4O_3Rh$: C 70.50, H 4.70, N 6.71; found C 70.48, H 4.71, N 6.70

[5, 10 – dimesityl – 19 – (4 – phenylacetylenylphenyl) – 25 – oxasmaragdyrin]dicarbonyl rhodium-(I) 5c: ^1H NMR (400 MHz, $CDCl_3$) δ 9.48 (m, 2H), 9.185 (d, J = 4.4 Hz, 2H), 8.76 (d, J = 4.4 Hz, 2H), 8.67 (s, 2H), 8.44 (m, 2H), 8.28 (d, J = 7.80 Hz, 2H), 7.98 (d, J = 7.80 Hz, 2H), 7.71 (m, 2H), 7.46 (m, 3H), 7.26 (s, 4H), 2.66 (s, 6H), 1.99 (s, 6H), 1.86 (s, 6H), - 1.60 (s, 2H); IR (KBr): ν_{max}/ cm^{-1} = 2007, 2072 (CO); UV / Vis (in CH_2Cl_2): λ_{max} [nm] (ε x 10^{-4} $M^{-1}cm^{-1}$) = 462 (16.8), 480 (sh, 8.9), 578 (1.25), 620 (1.28), 640 (1.12), 703 (1.5); FAB-MS m/z (%) = 934 (25) [M^+]; elemental analysis: calcd (%) for $C_{57}H_{43}N_4O_3Rh$: C 73.23, H 4.63, N 5.99. Found C 73.25, H 4.62, N 5.94.

[5, 10 – dimesityl – 19 – (3– phenylacetylenylphenyl) – 25 – oxasmaragdyrin]dicarbonyl rhodium-(I) 5d: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.49 (m, 2H), 9.17 (d, J = 4.4 Hz, 2H), 8.75 (d, J = 4.4 Hz, 2H), 8.67 (s, 2H), 8.44 (m, 2H), 7.92 (m, 1H), 7.78 (m, 3H), 7.61 (m, 2H), 7.32 (m, 3H), 7.26 (s, 4H), 2.65 (s, 6H), 1.99 (s, 6H), 1.86 (s, 6H), - 1.59 (s, 2H); IR (KBr): ν_{max}/ cm^{-1} = 2007, 2072 (CO); UV / Vis (in CH_2Cl_2): λ_{max}[nm] (ε x 10^{-4} $M^{-1}cm^{-1}$) = 460 (6.29), 479 (sh, 3.5), 574 (0.52), 619 (0.55), 639 (0.49), 701 (0.19); FAB-MS m/z (%) = 934 (25) [M^+]

[5, 10 – dimesityl – 19 – [4 – ((phenylacetylenyl) phenylacetylenyl) phenyl] – 25 – oxasmaragdyrin] dicarbonyl rhodium-(I) 5e: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.56 (m, 2H), 9.17 (d, J = 4.4 Hz, 2H), 8.86 (d, J = 4.4 Hz, 2H), 8.76 (s, 2H), 8.58 (m, 2H), 8.41 (d, J = 8.08 Hz, 2H), 8.02 (d, J = 8.08 Hz, 2H), 7.56 (m, 6H), 7.41 (m, 3H), 7.26 (s, 4H), 2.65 (s, 6H), 1.92 (s, 12H), -1.61 (s, 2H); IR (KBr): ν_{max}/ cm^{-1} = 2007, 2072 (CO); UV / Vis (in CH_2Cl_2): λ_{max} [nm] (ε x 10^{-4} $M^{-1}cm^{-1}$); 463 (5.7), 479 (sh, 1.37), 617 (0.31), 646 (0.29), 703 (0.82); FAB-MS m/z (%) = 1034 (25) [M^+].

[5, 10 – dimesityl – 19 – [3– ((phenylacetylenyl) phenylacetylenyl) phenyl] – 25 – oxasmaragdyrin] dicarbonyl rhodium-(I) 5f: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.50 (m, 2H), 9.21 (d, J = 4.4 Hz, 2H), 8.81 (d, J = 4.4 Hz, 2H), 8.73 (s, 2H), 8.43 (m, 2H), 8.42 (d, 2H, J =8.4 Hz), 8.03 (d, 2H, J = 8 Hz), 7.89 (S, 1H), 7.50 – 7.54 (m, 4H), 7.35 – 7.38 (m, 4H), 7.26 (S, 4H), 2.66 (S, 4H), 1.99 (S, 6H), 1.86 (S, 6H), - 1.61 (S, 2H); IR (KBr): ν_{max}/ cm^{-1} = 2007, 2072 (CO); UV /Vis (in CH_2Cl_2): λ_{max} [nm] (ε x 10^{-4} $M^{-1}cm^{-1}$); 462 (6.1), 481 (sh, 2.8), 581 (0.32), 620 (0.38), 705(0.54); FAB-MS m/z (%) = 1034 (25) [M^+].

[5, 10 – dimesityl – 19 – (4 – ferrocenylacetylenylphenyl) – 25 – oxasmaragdyrin] dicarbonyl rhodium-(I) 5h : ^{1}H NMR ($CDCl_3$, 400 MHz, 25°C): δ = 9.51 (m, 2H), 9.18 (d, J = 4.6 Hz, 2H), 8.76 (d, J = 4.6 Hz, 2H),8.68 (s, 2H), 8.44 (m, 2H), 8.30 (d, J = 7.6 Hz, 2H), 8.01 (d, J = 8.0 Hz, 2H), 7.26 (s, 4H), 4.67 (t, J =1.6 Hz, 2H), 4.34 (t, J = 1.6 Hz, 2H), 4.04 (s, 5H), 2.66 (s, 6H), 2.11 (s, 6H), 1.99 (s, 6H), -1.61 (s, 2H); IR (KBr): ν_{max}/ cm^{-1} = 2007, 2072 (CO); UV/Vis (CH_2Cl_2): λ_{max} (ε x 10^{-4} $M^{-1}cm^{-1}$); 462 (18.5), 480 (1.5), 619 (0.8), 701 (1.1): m/z (%): 1044 (40) [$(M+2)^+$]**;** elemental analysis: calcd (%) for $C_{61}H_{47}N_4O_3FeRh$: C 70.25, H 4.54, N 5.37; found C 70.24, H 4.55, N 5.37.

[5, 10 – dimesityl – 19 – (3 – ferrocenylacetylenylphenyl) – 25 – oxasmaragdyrin] dicarbonyl rhodium-(I) 5i : ^{1}H NMR ($CDCl_3$, 400 MHz, 25°C): δ = 9.49 (m, 2H), 9.26 (d, J = 4.4 Hz, 2H), 8.89 (d, J = 4.4 Hz, 2H), 8.68 (s, 2H), 8.28 (m, 2H), 7.88 (m, 1H), 7.78 (m, 1H), 7.55 (m, 2H), 7.24 (s, 4H), 4.55 (t, J = 1.6 Hz, 2H), 4.25 (s, 7H), 2.64 (s, 6H), 1.95 (s, 12H), -1.64 (s, 2H); IR (KBr): ν_{max}/ cm^{-1} = 2007, 2072 (CO)**;** UV/Vis (CH_2Cl_2): λ_{max} (ε x 10^{-4} $M^{-1}cm^{-1}$); 460 (18.2), 480 (1.6), 578 (1.3), 618 (1.4), 637 (1.4), 700 (1.6); m/z (%): 1044 (40) [$(M+2)^+$]; elemental analysis: calcd (%) for $C_{61}H_{47}N_4O_3FeRh$: C 70.25, H 4.54, N 5.37; found C 70.26, H 4.55, N 5.38.

[5, 10 – dimesityl – 19 – [4 –(Ferrocenylphenylacetylenyl)phenyl] – 25 – oxasmaragdyrin] dicarbonyl rhodium-(I) 5j: ^{1}H NMR ($CDCl_3$, 400 MHz, 25°C): δ = 9.47 (m, 2H), 9.25 (d, J = 4.5 Hz, 2H), 8.80 (d, J = 4.5 Hz, 2H), 8.62 (s, 2H), 8.59 (m, 2H), 8.37 (d, 2H), 8.02 (d, 2H), 7.62 (d, J = 8.1Hz, 2H), 7.50 (d, J = 8.1Hz, 2H), 7.34 (m, 4H), 4.73 (d, 2H), 4.39 (s, 2H), 4.09 (s, 5H), 2.65 (s, 6H), 1.92 (s, 12H), - 1.89 (s, 2H); ; IR (KBr): ν_{max}/ cm^{-1} = 2007, 2072 (CO); UV/Vis (CH_2Cl_2): λ_{max} (ε x 10^{-4} $M^{-1}cm^{-1}$); 462 (19.8), 480 (1.6), 572 (1.4), 619 (0.7), 703 (1.2); FAB-MS: m/z (%): 1118 (25) [M^+]**;**

elemental analysis: calcd (%) for $C_{67}H_{51}N_4O_3FeRh$: C 71.92, H 4.59, N 5.00; found: C 71.90, H 4.59, N 5.01.

[5, 10 – dimesityl – 19 – [3 –(Ferrocenylphenylacetylenyl)phenyl] – 25 – oxasmaragdyrin] dicarbonyl rhodium-(I) 5k : ^{1}H NMR ($CDCl_3$, 400 MHz, 25°C): δ = 9.47 (m, 2H), 9.23 (d, J = 4.4 Hz, 2H), 8.81 (d, J = 4.4 Hz, 2H), 8.63 (s, 2H), 8.40 (m, 2H), 7.93 (d, 1H), 7.70 – 7.78 (m, 2H), 7.46 – 7.39 (m, 5H), 7.26 (s, 4H), 4.67 (t, J = 1.6 Hz, 2H), 4.34 (t, J = 1.6 Hz, 2H), 4.04 (s, 5H), 2.65 (s, 6H), 2.02 (s, 12H), - 1.88 (s, 2H); IR (KBr): ν_{max}/ cm^{-1} = 2007, 2072 (CO); UV/Vis (CH_2Cl_2): λ_{max} (ε x 10^{-4} $M^{-1}cm^{-1}$); 463 (20.3), 481 (5.8), 574 (1.3), 653 (1.2), 722 (1.5); FAB-MS: m/z (%): 1118 (25) [M^+]**;** elemental analysis: calcd (%) for $C_{67}H_{51}N_4O_3FeRh$: C 71.92, H 4.59, N 5.00; found: C 71.91, H 4.57, N 5.01.

2. Measurement of two-photon absorption cross section (σ): Two-photon absorption cross-section measurement studies by open aperture Z-Scan technique for samples **4c – 4 f** and **5c – 5f** have been done by IMRA laser set up (for experimental details see reference7), while for experimental details of two-photon absorption cross section measurements for rest of the samples at 830 nm with the MIRA laser is here. Our femtosecond experimental scheme involves mode locked Coherent Mira titanium: sapphire laser (Model 900) which is pumped by Coherent Verdi frequency doubled Nd: vanadate laser. The model 900 Mira is tunable from 740 to 900 nm and its repetition rate is 76 MHz. The duration of the pulse is 150 fs as measured by autocorrelation technique. We controlled the average power of the laser pulse in the range of 10-20 mW by using a half wave plate and a polarizer as shown in Figure S1. In order to reduce the thermal effect which contribute to the $\sigma^{(2)}$ value, we have used a mechanical chopper in the laser path of Z-scan setup where frequency is as low as 200 Hz. The use of such chopper also reduces the scatter problem seen in some linearly absorbing samples. We used 830 & 860 nm wavelength here for the measurements. Using a 20 cm focal length lens, the beam is focused into a 1 cm long cell filled with sample, where it easily produces GW-level intensity at the focal point of the lens. We scan the sample through the focal point using a motorized translation stage (model ESP 300), which can step with a minimum resolution of 0.1μm. This allows a smooth intensity scan for the samples in this wavelength. The transmitted beam, after passing through the sample is focused into the aperture of a UV-enhanced amplified silicon photodetector (Thorlabs DET 210) by using a 7.5 cm focal length lens. We measure the signal in an oscilloscope (Tektronix TDS 224), which is finally interfaced with the computer using GPIB card (National

Instruments). The data is acquired using LabVIEW programming. We obtain the nonlinear absorption coefficient β, by fitting our measured transmittance values to the following formula:

$$\mathbf{T(z) = 1 - \beta I_0 L / (2(1+ z^2/z_0^2))}$$

Where, β = nonlinear absorption coefficient, I_0= on-axis electric field intensity at the focal point in absence of the sample, L= sample thickness, z_0 = Rayleigh range = $\pi w_0^2/\lambda$, w_0 is the minimum spot size at the focal point. The β values are obtained by curve fitting the measured open-aperture traces with the above equation.After we get the value of β, the TPA cross-section σ^2 (in units of 1GM = 10^{-50}cm^4.s/photon.molecule), of one solute molecule is given by the following expression:

$\mathbf{\sigma^2 = \beta.h\nu/N.c.10^{-3}}$,

Where ν is the frequency of the incident laser beam, N is Avagadro constant, c is the concentration of the compound in dichloromethane solvent. We have taken the known value of σ^2 for Rhodamine-6G as the reference for calibrating our measurement technique.

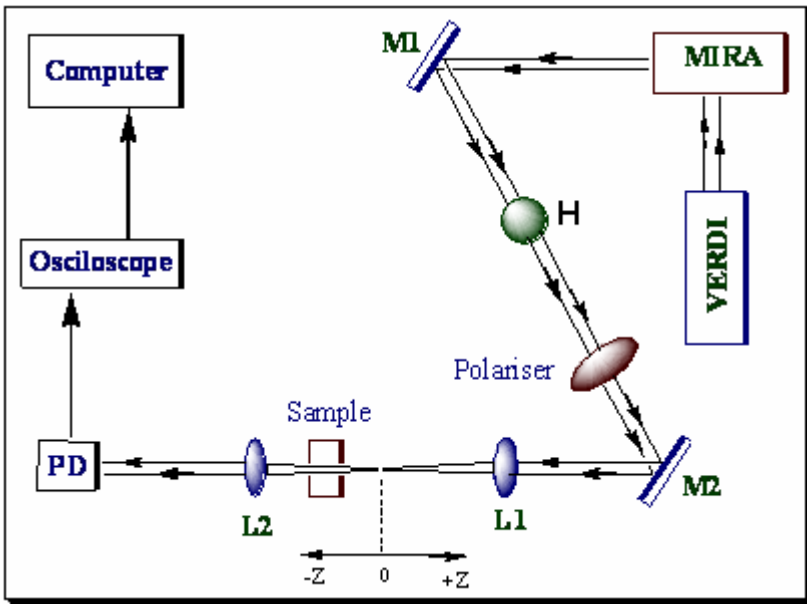


Figure S1. Experimental setup for two-photon absorption cross-section measurement.

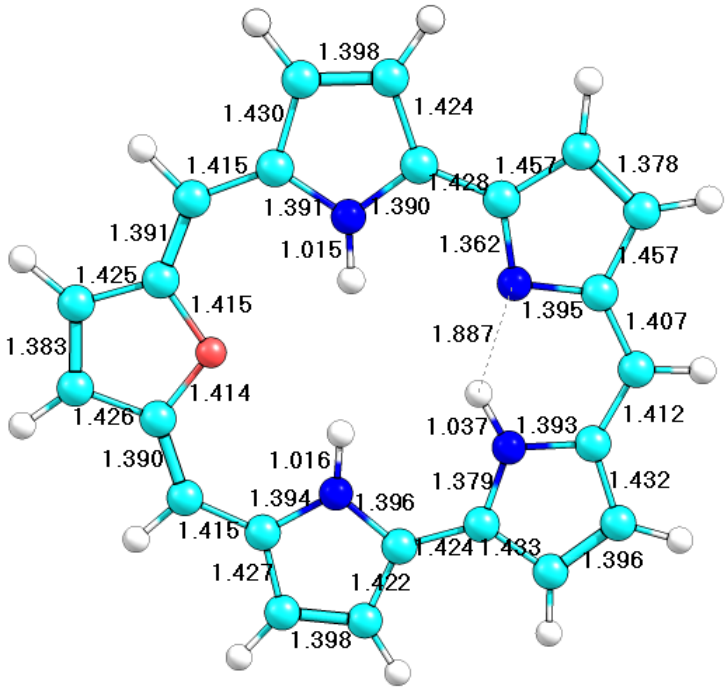
3. Computational method.

The geometry optimization of **4a** to **4e**, **4g**, **4h**, **4i**, and **5b** systems were done at the BLYP level of density functional theory[8,9] by using the Gaussian03 suit of programs.[10] The basis set selected for this study was 6-31G* for H, C, N and O atoms and LanL2DZ for Fe and Rh atoms.[11-14] When LanL2DZ basis set is used along with the 6-31G* basis set, the name Gen1 is used to designate it. This level of theory was chosen as a compromise between accuracy and applicability to large systems.

3.1 Optimized geometries at BLYP/6-31G(d) Level.

4a

E (SCF) = -1179.8592567 A. U.



Atomic number and the X, Y, and Z Cartesian coordinates in Å unit

8	-2.755160	-0.004647	0.000020
7	-0.630307	-2.269084	-0.000321
7	2.197056	-1.365610	0.000462
7	2.113773	1.338908	0.000140
7	-0.613151	2.280976	-0.000388
6	-1.824810	-2.988587	-0.000160
6	-1.453493	-4.366699	-0.000253
6	-0.058451	-4.451881	-0.000213
6	0.468386	-3.130948	-0.000117
6	1.823492	-2.693141	0.000037
6	3.033619	-3.460799	-0.000124
6	4.109880	-2.571232	0.000026
6	3.584431	-1.239564	0.000360
6	4.203328	0.029814	0.000316
6	3.506159	1.252275	0.000176
6	4.087619	2.588108	-0.000041
6	3.035361	3.477961	-0.000169
6	1.823450	2.669411	-0.000143
6	0.476480	3.143705	-0.000289
6	-0.054800	4.464675	-0.000147
6	-1.449226	4.371148	-0.000031
6	-1.810998	2.987343	-0.000083
6	-3.117969	2.445083	0.000041
6	-3.590210	1.137230	0.000125
6	-4.945530	0.695794	0.000273
6	-4.951819	-0.686872	0.000313
6	-3.599629	-1.138396	0.000099
6	-3.133053	-2.448162	-0.000045
1	5.296112	0.057446	0.000350
1	-0.595593	-1.253887	0.001011
1	1.643360	-0.488687	-0.000116
1	-0.524484	1.270046	0.000221
1	-2.162064	-5.193322	-0.000432
1	0.543419	-5.358309	-0.000375
1	3.081653	-4.548058	-0.000324
1	5.168949	-2.824459	-0.000035
1	5.154039	2.815971	-0.000032
1	3.081984	4.566708	-0.000310
1	0.541961	5.374480	-0.000119
1	-2.164808	5.192036	0.000040
1	-3.915857	3.192886	0.000165
1	-5.804844	1.364481	0.000374
1	-5.816711	-1.348240	0.000454
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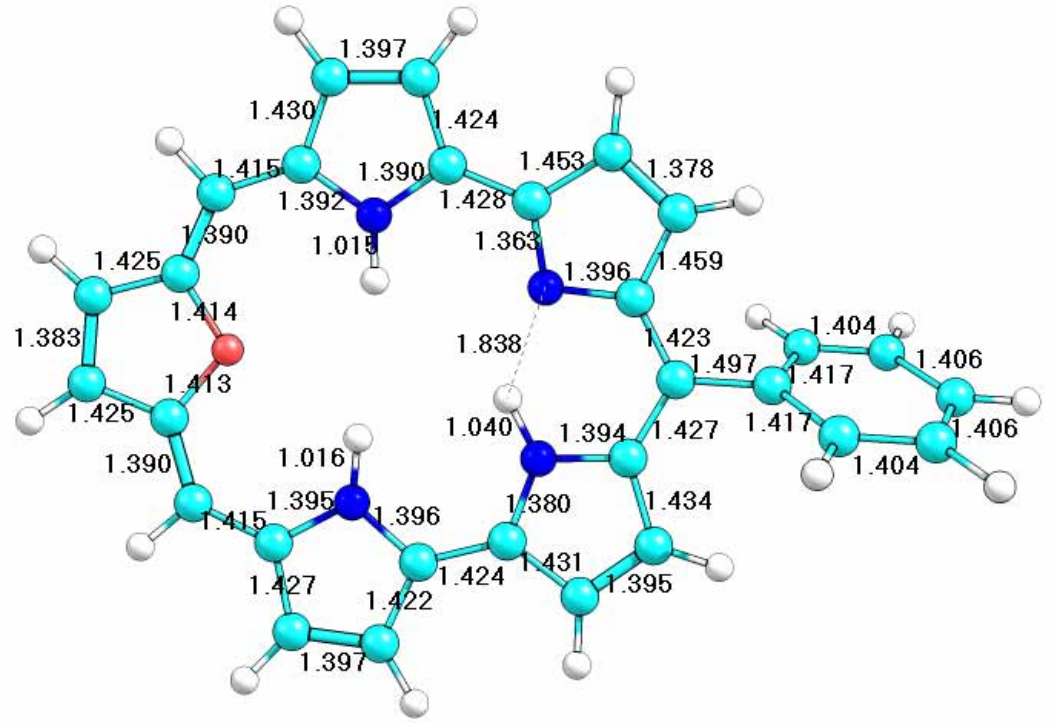
4b

E(SCF) = -1410.8075998 a.u.



Atomic number and the X, Y, and Z Cartesian coordinates in Å unit

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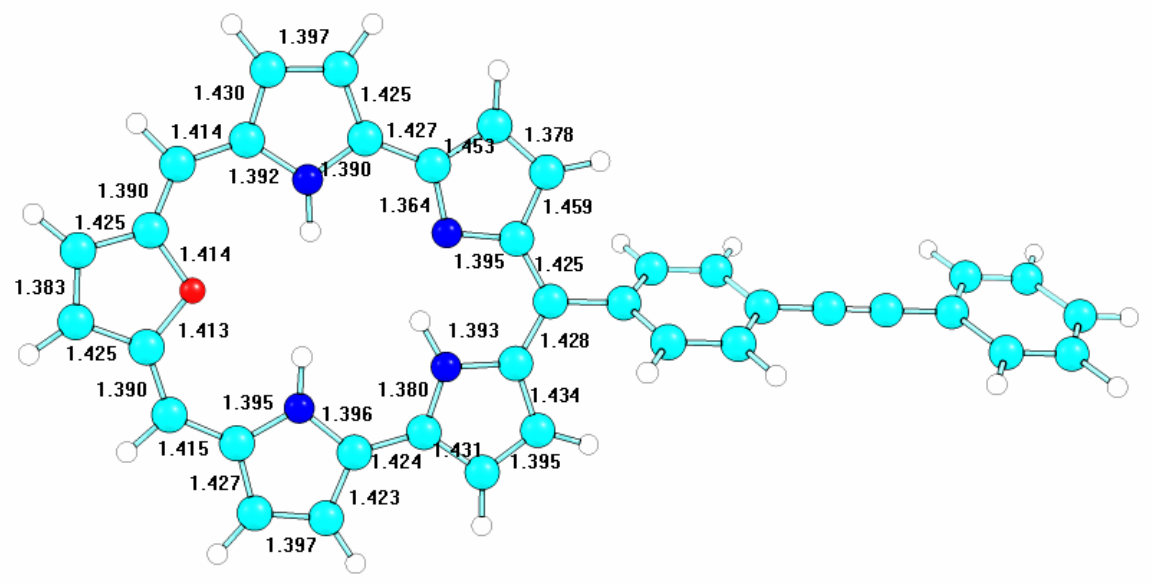
7	-0.881719	1.303482	0.019903
7	1.873164	2.259918	-0.009319
6	3.119314	-2.962205	0.039618
6	2.748549	-4.339384	0.085057
6	1.353975	-4.424929	0.075518
6	0.826593	-3.104976	0.021584
6	-0.533259	-2.681078	0.007067
6	-1.723901	-3.473393	0.066531
6	-2.818879	-2.608931	0.060510
6	-2.325166	-1.265153	-0.014166
6	-2.991127	-0.003162	-0.007422
6	-2.274972	1.226607	-0.010072
6	-2.837963	2.569837	-0.098664
6	-1.775403	3.446748	-0.113274

6	-0.575107	2.630191	-0.041807
6	0.771178	3.105932	-0.049805
6	1.284005	4.433427	-0.108116
6	2.679075	4.361199	-0.098705
6	3.061082	2.984757	-0.037161
6	4.376248	2.463886	-0.020096
6	4.863957	1.162305	0.002463
6	6.222435	0.731695	0.017339
6	6.239026	-0.651130	0.034103
6	4.890257	-1.112298	0.029695
6	4.427821	-2.423009	0.042651
1	-7.139085	1.204942	1.840935
6	-7.328509	0.004892	0.040248
6	-6.607643	0.680885	1.040707
6	-4.487788	0.002590	0.006812
6	-5.203316	0.679822	1.025249
6	-5.228481	-0.675161	-0.993301
6	-6.632831	-0.672800	-0.976775
1	1.889079	-1.229620	-0.057648
1	-0.402363	-0.469905	-0.041416
1	1.804343	1.250158	0.063399
1	3.457434	-5.164765	0.125146
1	0.752209	-5.330800	0.106560
1	-1.748944	-4.560216	0.117023
1	-3.868584	-2.885902	0.115151
1	-3.896346	2.813939	-0.161446
1	-1.812168	4.533908	-0.177459
1	0.673805	5.332966	-0.154727
1	3.382678	5.191455	-0.137595
1	5.163078	3.223111	-0.033518
1	7.076720	1.406783	0.015500
1	7.108804	-1.305902	0.047675
1	5.225714	-3.170070	0.064627
1	-8.422507	0.006102	0.053046
1	-4.646787	1.191587	1.814605
1	-4.692603	-1.187261	-1.796943
1	-7.183966	-1.194954	-1.764961

4c

E(SCF) = -1717.8970662 a.u.



Atomic number and the X, Y, and Z Cartesian coordinates in Å unit

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7	1.364852	1.302948	-0.015508
7	4.123185	2.257103	-0.047073
6	5.366987	-2.960444	0.104926
6	4.994919	-4.336490	0.173145
6	3.600571	-4.421174	0.159062
6	3.074403	-3.101814	0.079012
6	1.714645	-2.678732	0.050818
6	0.525116	-3.470491	0.129909
6	-0.570759	-2.607743	0.101326
6	-0.078728	-1.265624	-0.008960
6	-0.745691	-0.002757	-0.032146
6	-0.027488	1.227540	-0.057292
6	-0.586837	2.568999	-0.188973
6	0.477415	3.443590	-0.214675
6	1.675055	2.627524	-0.108870
6	3.021491	3.101659	-0.115364
6	3.534745	4.428098	-0.197161
6	4.929347	4.356661	-0.173799
6	5.311160	2.981709	-0.080322

6	6.626122	2.462155	-0.042920
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6	-11.306089	0.781229	0.972357
6	-9.184319	0.001926	0.024376
6	-9.904808	0.787017	0.966931
6	-9.916231	-0.785206	-0.907631
6	7.113768	1.161143	0.006967
6	8.471893	0.730821	0.038986
6	8.487903	-0.651630	0.079746
6	7.139144	-1.112316	0.073958
6	6.675725	-2.422469	0.106428
6	-11.317449	-0.783516	-0.892624
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6	-5.103742	0.005191	-0.005265
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6	-2.238664	0.003656	-0.025808
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6	-2.980469	-0.738167	-0.981527
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1	2.997957	-5.325956	0.202461
1	0.500897	-4.555542	0.209719
1	-1.619434	-2.886054	0.166468
1	-1.643221	2.814796	-0.273922
1	0.443020	4.528570	-0.309138
1	2.924748	5.326219	-0.267485
1	5.633146	5.186138	-0.223744
1	7.412851	3.221256	-0.064786
1	-13.112396	-0.003779	0.053041
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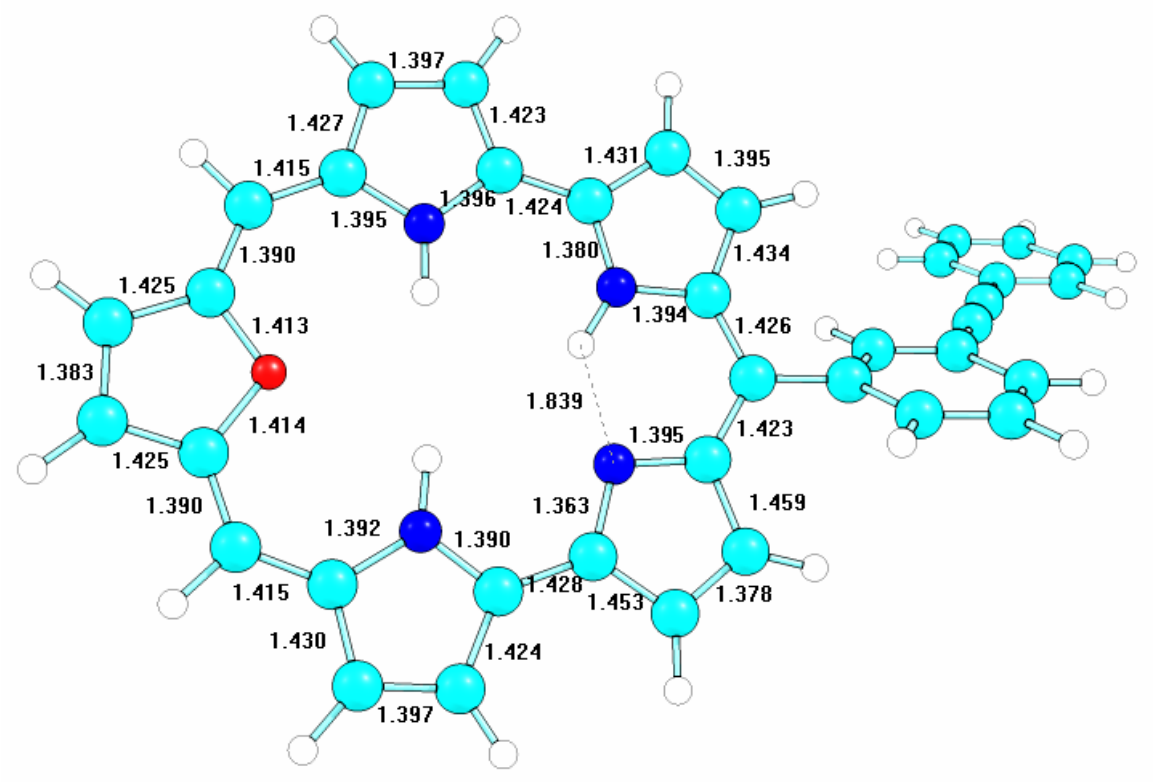
1	-9.369500	-1.390855	-1.634735
1	9.326395	1.405570	0.031269
1	9.357352	-1.306234	0.110631
1	7.472867	-3.169555	0.146604
1	-11.865837	-1.394441	-1.615927
1	-4.903357	1.319439	1.715674
1	-2.417246	1.306882	1.701540
1	-2.444975	-1.300049	-1.751019
1	-4.929979	-1.308340	-1.729725

4d

E(SCF) = -1717.896265 a.u.



Atomic number and the X, Y, and Z Cartesian coordinates in Å unit

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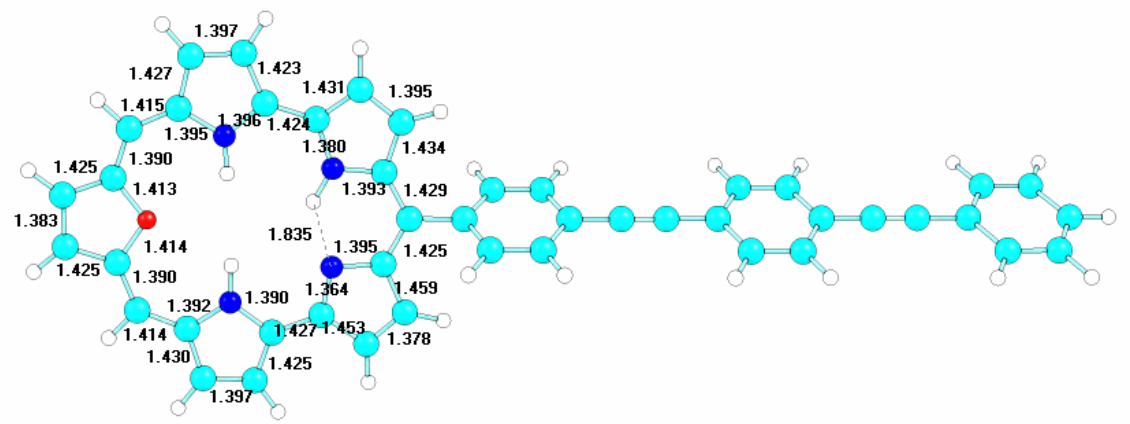
7	1.370298	-1.696247	-0.172822
7	4.161315	-1.854041	0.658733
6	4.213821	3.407310	-0.401195
6	3.579928	4.601136	-0.859371
6	2.247969	4.308974	-1.163116
6	2.022661	2.929462	-0.898692
6	0.832205	2.165720	-1.065242
6	-0.443954	2.583608	-1.561086
6	-1.288071	1.473164	-1.572270
6	-0.551993	0.348974	-1.072032
6	-0.902302	-1.023746	-0.905350
6	0.035400	-1.992840	-0.450943
6	-0.227241	-3.396807	-0.152469

6	0.958152	-3.936938	0.296016
6	1.929638	-2.856004	0.275029
6	3.296939	-2.942354	0.676455
6	4.051602	-4.048713	1.161656
6	5.350733	-3.607319	1.423257
6	5.428330	-2.214614	1.108032
6	6.557315	-1.372247	1.237242
6	-10.055580	1.929807	2.231110
6	-10.291827	0.926455	1.272677
6	-7.878796	0.648886	0.945579
6	-9.219294	0.289618	0.633821
6	-7.653386	1.664162	1.915960
6	6.740299	-0.014535	1.000916
6	7.928083	0.755825	1.164556
6	7.647296	2.064817	0.816987
6	6.277704	2.138020	0.428935
6	5.561305	3.249747	0.001083
6	-8.733593	2.294159	2.548580
6	-6.782354	0.004928	0.298050
6	-5.837849	-0.549180	-0.259612
6	-4.962957	-2.215824	-1.868255
6	-3.874173	-2.837775	-2.492995
6	-2.304161	-1.437551	-1.231754
6	-2.557216	-2.457039	-2.183921
6	-3.404772	-0.814952	-0.604281
6	-4.740571	-1.189703	-0.909799
1	3.402868	1.458224	-0.136851
1	1.422545	0.120017	-0.454569
1	3.896008	-0.931302	0.330294
1	4.079104	5.564241	-0.952076
1	1.495347	4.997582	-1.541449
1	-0.690359	3.595262	-1.877530
1	-2.321513	1.444533	-1.907983
1	-1.186591	-3.900630	-0.250234
1	1.141472	-4.961892	0.617266
1	3.660226	-5.054490	1.299249
1	6.182073	-4.195937	1.808297
1	7.458271	-1.876426	1.597498
1	-10.895842	2.424135	2.727266
1	-11.317308	0.638897	1.022044
1	-9.400165	-0.489744	-0.110702
1	-6.625924	1.944839	2.160678
1	8.877787	0.348317	1.507390
1	8.326445	2.915757	0.826021
1	6.154914	4.167055	-0.035571
1	-8.543644	3.073095	3.293062

1	-5.987734	-2.509169	-2.108492
1	-4.050971	-3.621999	-3.235167
1	-1.714591	-2.934365	-2.689836
1	-3.231761	-0.040390	0.145726

4e

E(SCF) = -2024.9870131 a.u.



Atomic number and the X, Y, and Z Cartesian coordinates in Å unit

8	8.914884	-0.009594	-0.039291
7	6.797401	2.242166	-0.096799
7	3.936230	1.362042	0.016058
7	3.993499	-1.302897	0.043029
7	6.753744	-2.252677	0.087174
6	7.990602	2.961786	-0.169246
6	7.616546	4.335918	-0.262187
6	6.222165	4.418902	-0.248607
6	5.697896	3.100427	-0.144041
6	4.338732	2.676340	-0.106473
6	3.148418	3.464971	-0.202479
6	2.053459	2.601977	-0.154546
6	2.546829	1.263046	-0.014708
6	1.881260	0.000054	0.037064
6	2.601304	-1.228722	0.087324
6	2.044575	-2.567884	0.250478
6	3.110282	-3.440087	0.291699
6	4.306223	-2.624742	0.164120
6	5.653221	-3.096849	0.175864
6	6.168225	-4.420985	0.281919
6	7.562567	-4.348638	0.252275
6	7.942606	-2.975289	0.130673
6	9.256809	-2.455239	0.079201

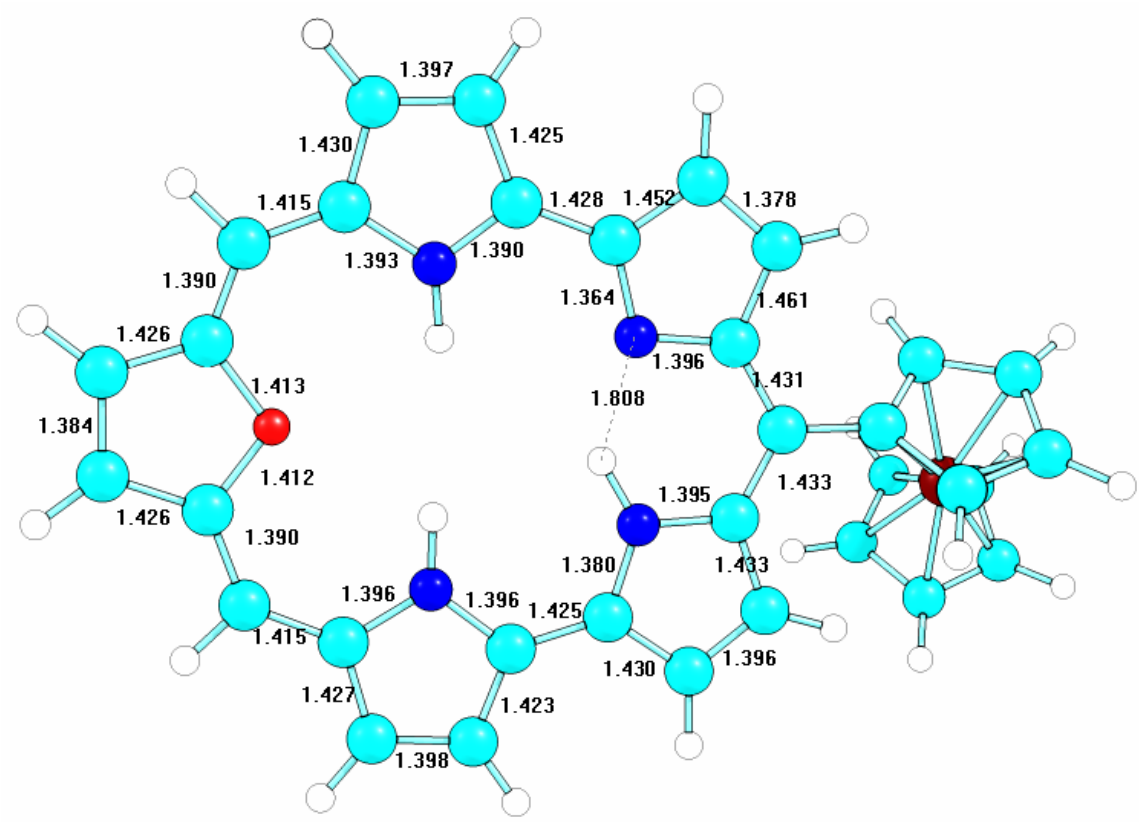
6	-9.411421	-0.006615	-0.007887
6	-8.677990	-0.830512	-0.909177
6	-6.553228	-0.012286	0.003224
6	-7.283023	-0.833005	-0.904153
6	-7.286865	0.811116	0.905112
6	9.742824	-1.154831	0.003106
6	11.100313	-0.723611	-0.040245
6	11.114482	0.657878	-0.106990
6	9.765201	1.116900	-0.106791
6	9.299993	2.425663	-0.162815
6	-8.681780	0.814194	0.899294
6	-5.130704	-0.014216	0.008634
6	-3.900380	-0.014787	0.013714
6	-2.476644	-0.013581	0.020710
6	-1.738075	-0.784678	-0.919699
6	0.388687	-0.008276	0.034300
6	-0.339950	-0.778350	-0.909369
6	-0.352046	0.760031	0.970149
6	-1.750173	0.760142	0.968392
6	-16.324179	0.014657	-0.034123
6	-15.616964	-0.829385	-0.910963
6	-13.490113	0.004997	-0.023399
6	-14.215796	-0.838343	-0.910230
6	-14.216737	0.853231	0.857989
6	-15.617898	0.853850	0.848104
6	-12.064282	0.000394	-0.018095
6	-10.834456	-0.003263	-0.013549
1	6.764407	1.230725	-0.009808
1	4.469456	0.469509	0.041542
1	6.683483	-1.246496	-0.023474
1	8.323442	5.160758	-0.334855
1	5.618271	5.321964	-0.307338
1	3.123059	4.547928	-0.306553
1	1.004641	2.878065	-0.226239
1	0.989049	-2.813820	0.345064
1	3.077890	-4.522751	0.410260
1	5.559425	-5.318194	0.371635
1	8.267429	-5.176268	0.315887
1	10.044465	-3.212909	0.113425
1	-9.224393	-1.465628	-1.610791
1	-6.733715	-1.470078	-1.601698
1	-6.740457	1.445943	1.606977
1	11.955692	-1.397029	-0.021743
1	11.983042	1.312823	-0.152142
1	10.096079	3.172877	-0.218379
1	-9.231144	1.451425	1.596669

1	-2.278537	-1.376985	-1.662363
1	0.207079	-1.360625	-1.654799
1	0.184394	1.344011	1.722246
1	-2.300065	1.349567	1.706435
1	-17.417985	0.018397	-0.038278
1	-16.160567	-1.483869	-1.598855
1	-13.664424	-1.492696	-1.590065
1	-13.666081	1.503819	1.542009
1	-16.162214	1.512035	1.531891

3.2 Optimized geometries at BLYP/Gen1 Level.

4g

E(SCF) = -1688.9355558 a.u.



Atomic number and the X, Y, and Z Cartesian coordinates in Å unit

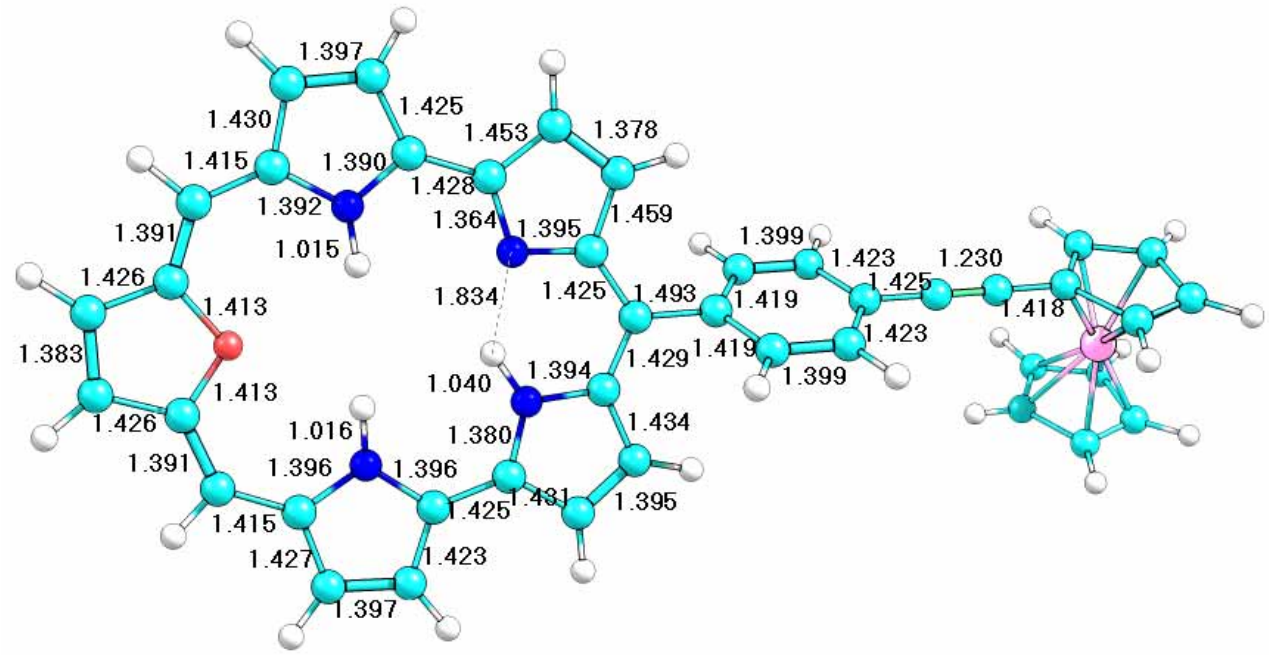
8	5.205410	-0.334041	0.252642
7	2.860952	-2.278577	-0.236958

7	0.130075	-1.040342	-0.521756
7	0.484093	1.564296	-0.223746
7	3.337179	2.151846	0.139936
6	3.943927	-3.151848	-0.116755
6	3.406678	-4.466778	-0.250642
6	2.026469	-4.365025	-0.445648
6	1.675143	-2.986407	-0.438621
6	0.384865	-2.395357	-0.572346
6	-0.876775	-3.045851	-0.745167
6	-1.867623	-2.063512	-0.773809
6	-1.236923	-0.784303	-0.631797
6	-1.758605	0.550008	-0.588246
6	-0.888423	1.677428	-0.453595
6	-1.237996	3.088322	-0.596378
6	-0.074557	3.809368	-0.439263
6	0.977270	2.835469	-0.209963
6	2.360802	3.129611	-0.014310
6	3.032237	4.384322	0.052356
6	4.393237	4.139557	0.251771
6	4.595762	2.725232	0.305339
6	5.826452	2.046573	0.468933
26	-4.925247	-0.025708	0.244926
6	-5.039162	-0.289723	2.313748
6	-6.361621	-0.228046	1.743705
6	-6.487616	-1.302106	0.791623
6	-5.242472	-2.027330	0.773748
6	6.151873	0.695105	0.455655
6	7.434589	0.093932	0.616300
6	7.286461	-1.277523	0.510081
6	5.907420	-1.559177	0.282256
6	5.294879	-2.794744	0.108798
6	-4.348419	-1.402090	1.715244
6	-4.003693	1.804791	-0.076249
6	-5.332925	1.809724	-0.627299
6	-5.402696	0.769205	-1.620187
6	-4.117314	0.128041	-1.682716
6	-3.216085	0.784148	-0.748344
1	2.960006	-1.267802	-0.226847
1	0.748958	-0.218880	-0.358968
1	3.137476	1.157933	0.181835
1	3.997494	-5.379624	-0.196747
1	1.320587	-5.183064	-0.572523
1	-1.020036	-4.121315	-0.830141
1	-2.936069	-2.223440	-0.871479
1	-2.222359	3.485787	-0.829190
1	0.047958	4.890551	-0.495322

1	2.546918	5.353431	-0.041554
1	5.189887	4.876529	0.341068
1	6.688941	2.702293	0.616491
1	-4.625972	0.398874	3.049715
1	-7.120915	0.520334	1.968121
1	-7.362268	-1.514700	0.177904
1	-5.019546	-2.895177	0.154286
1	8.353455	0.651781	0.789126
1	8.062469	-2.037911	0.580218
1	5.984955	-3.640893	0.163984
1	-3.317712	-1.695483	1.908305
1	-3.643525	2.444394	0.726403
1	-6.153167	2.453855	-0.312734
1	-6.279963	0.497977	-2.206830
1	-3.841489	-0.681374	-2.355991

4h

E(SCF) = -1996.0193641 a.u.



Atomic number and the X, Y, and Z Cartesian coordinates in Å unit

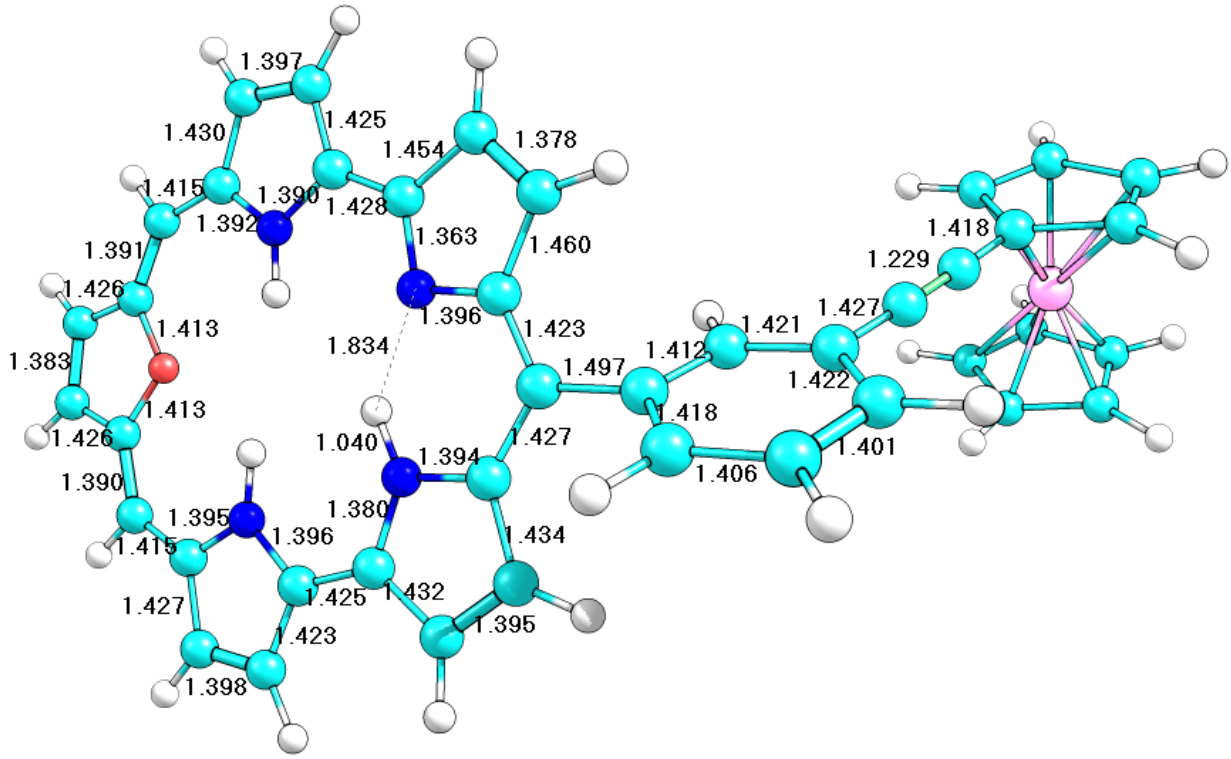
8	-7.961293	0.293284	0.200551
7	-5.673022	2.350582	-0.091340
7	-2.902079	1.222117	-0.269767
7	-3.169221	-1.416851	-0.011382
7	-5.993037	-2.127655	0.192178

6	-6.797537	3.173983	-0.019559
6	-6.309084	4.513928	-0.078704
6	-4.915877	4.474960	-0.180604
6	-4.507208	3.112143	-0.190136
6	-3.191056	2.571673	-0.261984
6	-1.938477	3.262397	-0.314511
6	-0.919777	2.308884	-0.332147
6	-1.525057	1.009428	-0.304004
6	-0.964391	-0.303693	-0.257123
6	-1.780873	-1.465447	-0.138632
6	-1.342357	-2.856472	-0.190247
6	-2.474255	-3.635323	-0.082828
6	-3.592118	-2.712744	0.022916
6	-4.970879	-3.067755	0.129630
6	-5.595514	-4.347217	0.178985
6	-6.975969	-4.153501	0.272683
6	-7.236795	-2.747118	0.279965
6	-8.500519	-2.114914	0.347956
26	8.878331	0.198195	0.206948
6	8.698357	0.949466	2.145389
6	10.069584	1.030009	1.707287
6	10.111769	1.853934	0.526031
6	8.766589	2.283339	0.234451
6	-8.877079	-0.776571	0.318469
6	-10.191706	-0.230034	0.391199
6	-10.092640	1.148019	0.319305
6	-8.713421	1.488932	0.200121
6	-8.143696	2.753373	0.099650
6	7.894903	1.726885	1.237049
6	8.283610	-1.794559	0.235886
6	9.636797	-1.695142	-0.236330
6	9.643276	-0.867618	-1.416153
6	8.294224	-0.451148	-1.680433
6	7.425489	-1.038734	-0.668082
6	6.015878	-0.910238	-0.588625
6	4.791988	-0.805920	-0.526670
6	3.373779	-0.686889	-0.462662
6	2.633425	-1.284639	0.595616
6	0.520469	-0.438373	-0.330919
6	1.241457	-1.160750	0.655459
6	1.262062	0.157247	-1.384527
6	2.653917	0.037179	-1.454335
1	-5.728212	1.336497	-0.099220
1	-3.503760	0.379876	-0.169195
1	-5.834142	-1.125693	0.210366
1	-6.940907	5.399744	-0.041729

1	-4.238839	5.324589	-0.239446
1	-1.821771	4.344259	-0.326016
1	0.150017	2.500036	-0.348039
1	-0.317190	-3.198516	-0.314696
1	-2.534855	-4.723179	-0.088825
1	-5.067134	-5.297591	0.143670
1	-7.747507	-4.920223	0.323988
1	-9.346101	-2.803261	0.430968
1	8.331302	0.382991	3.000278
1	10.920705	0.533923	2.172559
1	11.000500	2.089787	-0.058407
1	8.459974	2.900802	-0.608971
1	-11.097043	-0.827178	0.486927
1	-10.902328	1.875376	0.344846
1	-8.872934	3.567495	0.125127
1	6.811094	1.830989	1.271337
1	7.939080	-2.340203	1.112672
1	10.510620	-2.143811	0.234705
1	10.522517	-0.583081	-1.992990
1	7.958242	0.188955	-2.494443
1	3.168536	-1.837216	1.372183
1	0.695470	-1.610985	1.488166
1	0.729120	0.700164	-2.169366
1	3.203062	0.492879	-2.282311

4i

E(SCF) = -1996.01834902 a.u.



Atomic number and the X, Y, and Z Cartesian coordinates in Å unit

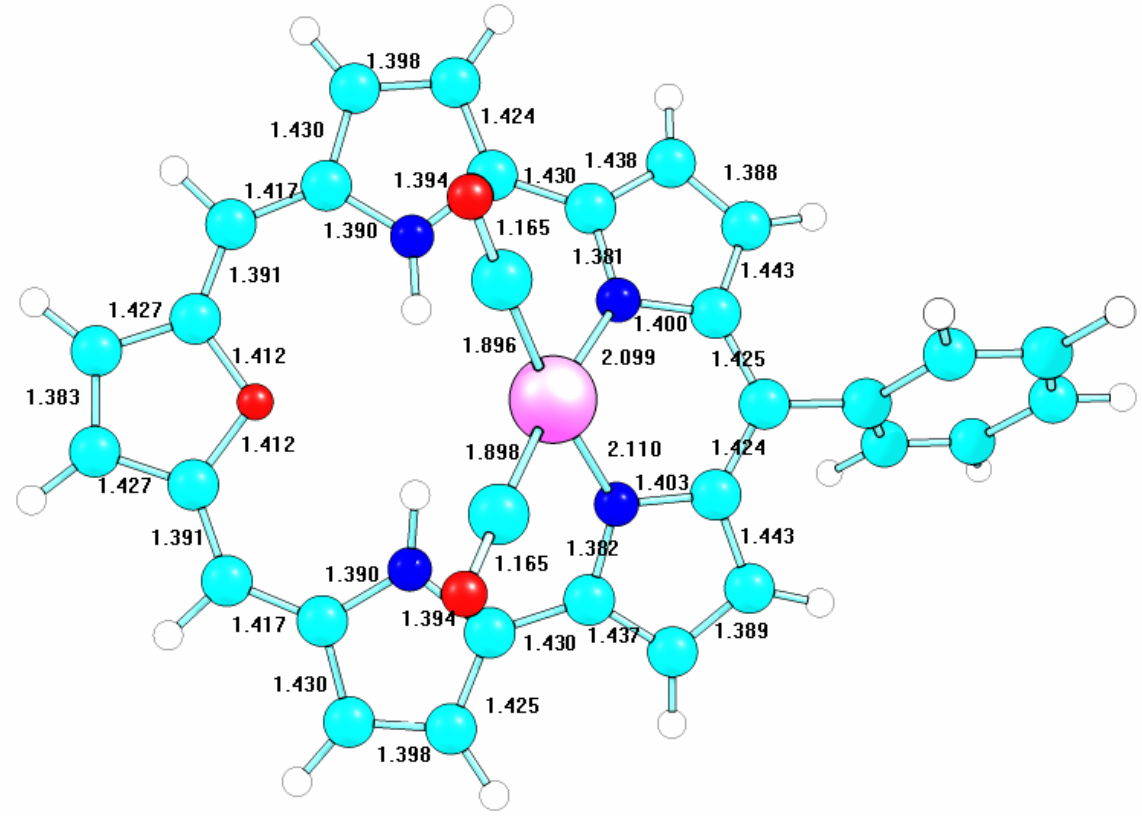
8	-7.007864	0.850394	-0.985398
7	-5.514583	-1.851486	-0.804168
7	-2.797526	-1.770369	0.453054
7	-2.340665	0.788046	1.042895
7	-4.661968	2.414302	0.349090
6	-6.706039	-2.218101	-1.431398
6	-6.602124	-3.618734	-1.686365
6	-5.363619	-4.065268	-1.217581
6	-4.671656	-2.954820	-0.658588
6	-3.374438	-2.908837	-0.071636
6	-2.418429	-3.963706	0.079880
6	-1.276902	-3.429493	0.678700
6	-1.510964	-2.035358	0.919038
6	-0.682292	-1.008600	1.463255
6	-1.110181	0.347196	1.532402

6	-0.399291	1.463601	2.147958
6	-1.206691	2.572061	2.013727
6	-2.405350	2.119828	1.326621
6	-3.535164	2.923102	0.984744
6	-3.781523	4.310679	1.193469
6	-5.045440	4.609886	0.678531
6	-5.611417	3.411014	0.141729
6	-6.880903	3.264386	-0.465468
26	7.582851	0.541877	-1.136557
6	6.751412	0.035299	-2.983962
6	8.085517	0.552159	-3.162492
6	8.992453	-0.294092	-2.429164
6	8.218564	-1.333945	-1.797597
6	-7.545569	2.157382	-0.981751
6	-8.839629	2.106995	-1.577716
6	-9.098579	0.797523	-1.941290
6	-7.970265	0.004390	-1.579807
6	-7.786199	-1.362644	-1.755157
6	6.835199	-1.131283	-2.143245
6	6.415929	2.042595	-0.292156
6	7.770449	2.497877	-0.436896
6	8.625827	1.615687	0.316287
6	7.804470	0.610193	0.931322
6	6.415319	0.873015	0.577555
6	5.276336	0.161032	1.031998
6	4.284165	-0.437518	1.442521
6	3.247426	-2.130993	2.924356
6	3.128071	-1.106286	1.945157
6	0.673510	-1.393606	1.968509
6	1.833006	-0.755717	1.476226
6	0.824143	-2.409549	2.946612
6	2.100070	-2.769862	3.413387
1	-5.323291	-0.905739	-0.487267
1	-3.113987	-0.780365	0.489755
1	-4.750718	1.448925	0.049864
1	-7.374073	-4.212856	-2.172551
1	-4.972262	-5.079397	-1.262652
1	-2.570889	-4.994358	-0.234283
1	-0.357907	-3.958878	0.916630
1	0.572943	1.411350	2.633297
1	-1.005392	3.585845	2.358527
1	-3.090264	4.998065	1.676487
1	-5.545149	5.577398	0.677416
1	-7.456678	4.191079	-0.539215
1	5.837490	0.464213	-3.393133
1	8.356665	1.442269	-3.729055

1	10.070007	-0.157197	-2.345709
1	8.608435	-2.121625	-1.154024
1	-9.486390	2.973145	-1.707717
1	-9.994029	0.404820	-2.420084
1	-8.630812	-1.861500	-2.237832
1	5.993681	-1.727495	-1.792174
1	5.528803	2.484095	-0.743089
1	8.096619	3.346366	-1.037187
1	9.711050	1.681193	0.384308
1	8.142819	-0.212103	1.559521
1	4.239384	-2.407134	3.290250
1	1.738643	0.016585	0.710243
1	-0.065607	-2.897070	3.352541
1	2.197686	-3.549960	4.174430

5b

E(SCF) = -1746.3438747 a.u.



Atomic number and the X, Y, and Z Cartesian coordinates in Å unit

45	-0.035396	-0.006100	1.170746
8	3.915243	-0.027464	-0.690758
8	1.004281	-2.188211	3.047049
8	1.089121	2.131290	3.053224
7	1.760602	-2.285260	-0.536328
7	-1.027967	-1.369424	-0.078856
7	-0.983846	1.390212	-0.095305
7	1.812721	2.271648	-0.502156
6	2.938850	-3.006950	-0.688938
6	2.550992	-4.381509	-0.766767
6	1.158476	-4.455890	-0.667039
6	0.654565	-3.132868	-0.509828
6	-0.694532	-2.668419	-0.408097
6	-1.886430	-3.383001	-0.776693
6	-2.941833	-2.484869	-0.697358
6	-2.403663	-1.211441	-0.283522
6	-3.073636	0.046120	-0.271273
6	-4.566457	0.040291	-0.416330
6	-5.209351	0.633843	-1.530466
6	-6.609085	0.609882	-1.650427
6	-7.395248	-0.009504	-0.662051
6	-6.770262	-0.611206	0.444896
6	-5.370477	-0.589984	0.564987
6	-2.375347	1.287292	-0.245871
6	-2.894047	2.610161	-0.497254
6	-1.815095	3.481900	-0.563289
6	-0.629599	2.706464	-0.324868
6	0.727799	3.143411	-0.426786
6	1.263642	4.460040	-0.519383
6	2.653427	4.357084	-0.629510
6	3.008210	2.971394	-0.619069
6	4.307566	2.415138	-0.717900
6	4.761646	1.100442	-0.752584
6	6.107486	0.640090	-0.867556
6	6.091262	-0.742415	-0.881547
6	4.735035	-1.173510	-0.775785
6	4.250653	-2.477719	-0.771870
6	0.634995	-1.365820	2.308771
6	0.686531	1.328871	2.310724
1	1.701815	-1.273324	-0.425397
1	1.730966	1.257503	-0.441898
1	3.246381	-5.210187	-0.891076
1	0.546300	-5.355349	-0.684543

1	-1.921367	-4.411252	-1.133621
1	-3.979381	-2.665534	-0.969162
1	-4.602487	1.096239	-2.313270
1	-7.084825	1.067721	-2.523053
1	-8.485067	-0.026944	-0.756199
1	-7.372323	-1.096147	1.219287
1	-4.887834	-1.052771	1.430142
1	-3.940920	2.854737	-0.658689
1	-1.840208	4.542142	-0.810976
1	0.674203	5.374160	-0.488813
1	3.368403	5.173982	-0.714241
1	5.110404	3.154032	-0.789586
1	6.974168	1.295628	-0.934741
1	6.942369	-1.416609	-0.962025
1	5.036051	-3.232558	-0.867206

3.3 HOMA index calculation

The HOMA model is widely used as a geometric criterion of aromaticity and using this model the local aromaticity of a molecule is easily determined from the bond length parameters (R_i) given in eq. 1.

$$\mathrm{HOMA} = 1 - \frac{\alpha}{n}\sum (R_{opt} - R_i)^2 \qquad (1)$$

where n is the number of bonds taken into the summation, R_{opt} = 1.388 Å, and α = 257.7. In this scale, the most aromatic system will have a HOMA value of 1.

3.4 MESP analysis

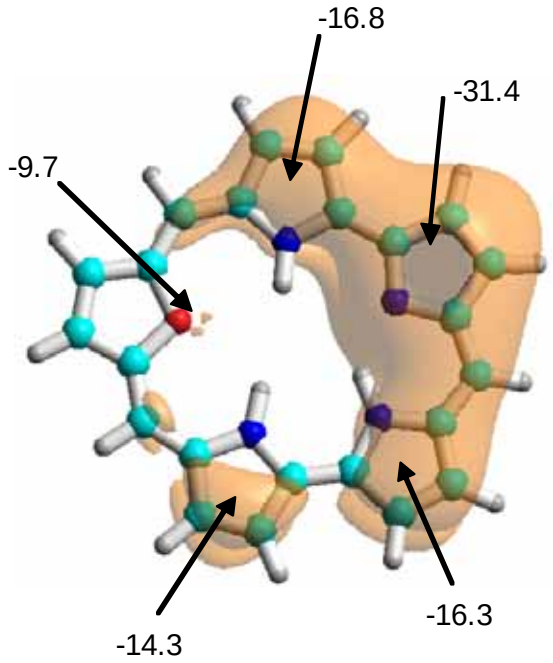
The molecular electrostatic potential (MESP) for the systems **4a** to **4e**, **4g**, **4h**, **4i**, and **5b** at their optimized level of theory using Gaussian 03 program. It is calculated rigorously from the electron density, $\rho(\mathbf{r})$ distribution by employing the equation

$$V(\mathbf{r}) = \sum_{A}^{N} \frac{Z_A}{|\mathbf{r} - \mathbf{R}_A|} - \int \frac{\rho(\mathbf{r}')d^3\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|} \qquad \text{--(2)}$$

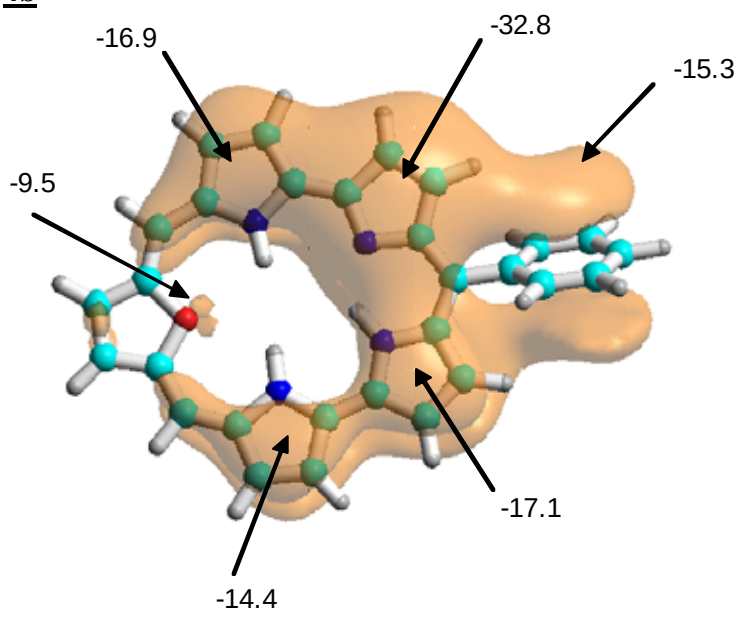
where Z_A is the charge on nucleus A, located at $\mathbf{R_A}$. Local minima of MESP (V_{min}) is often observed at the electron rich regions such as lone pair and π-bonded regions of molecules because at the electron rich regions, the electronic term in eq. 2 will be higher than the nuclear term.[15,16] Therefore, MESP analysis is often used for understanding aromaticity, the electrophilic reactive behavior of molecules, weak intermolecular interactions and molecular recognition phenomenon.[15-21] In the present work, the MESP analysis focusing on the evaluation of V_{min} value at various positions of the molecule will be done to explore the π-electron conjugation properties of the smaragdyrin systems. This type of an MESP-based approach for the study of π-electron conjugation features of condensed aromatic systems and the related sextet theory of aromaticity can be seen in the work of Suresh and Gadre.[21]

In all the cases, the MESP isosurface of value -7.0 kcal/mol is plotted below. The most negative valued point (V_{min}) obtained at the various regions are also depicted. All the values in kcal/mol.

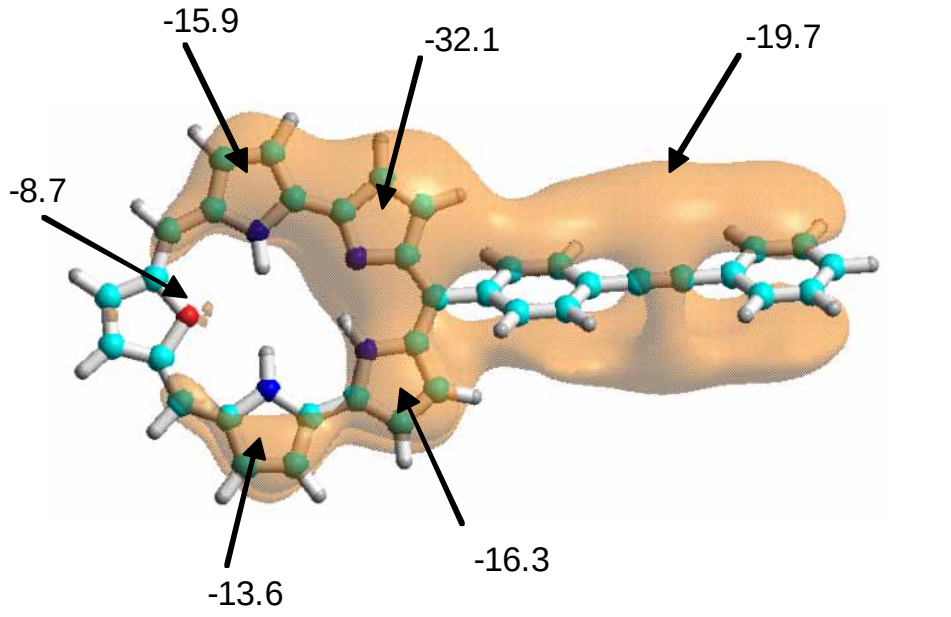
4a



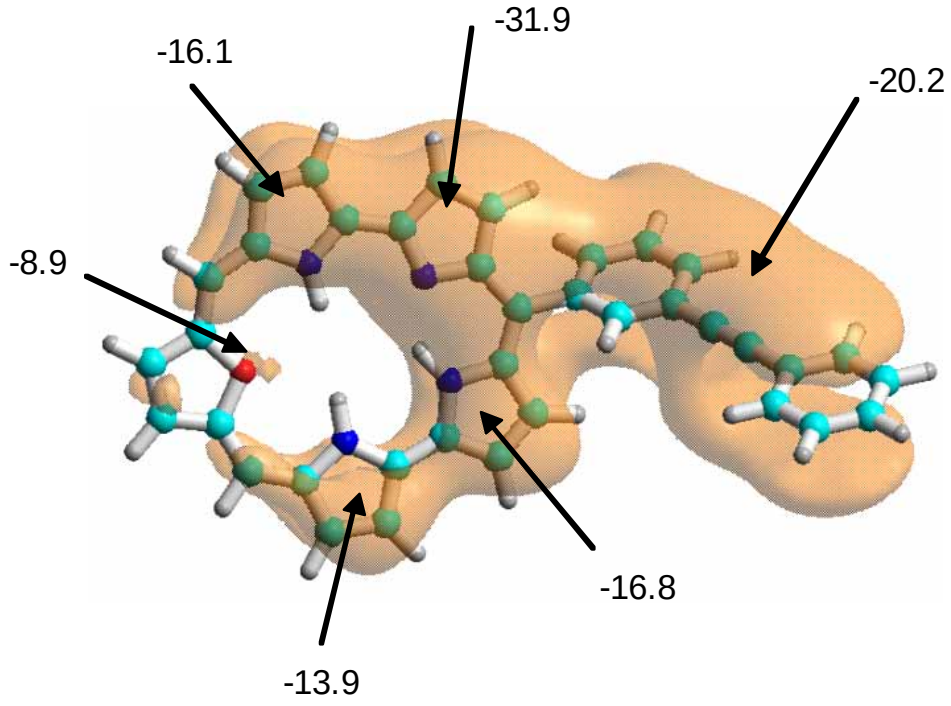
4b



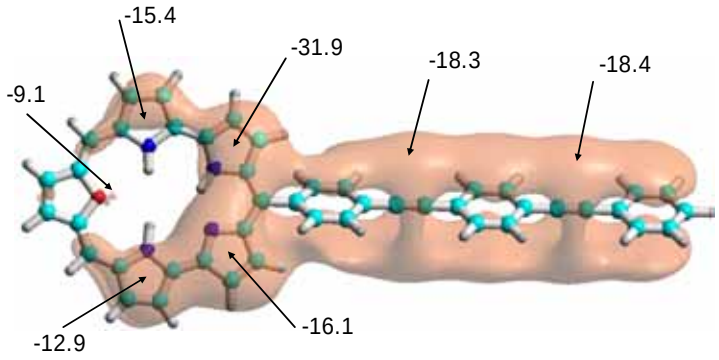
4c



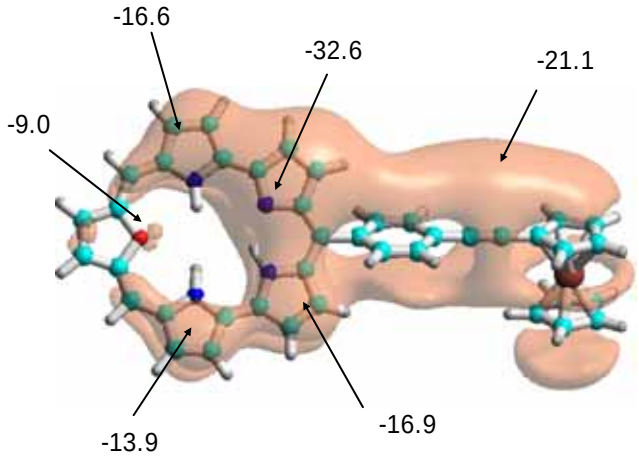
4d



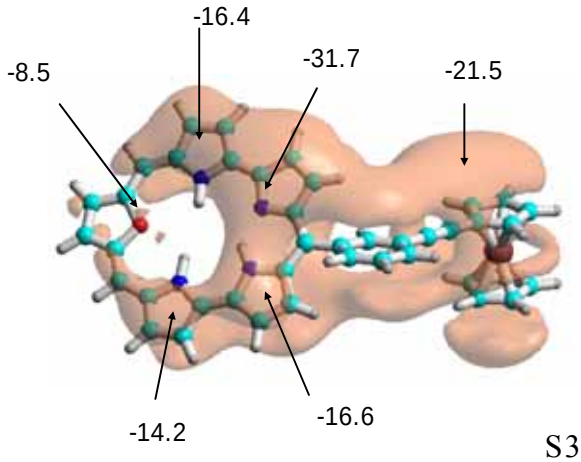
4e


-15.4
-31.9
-18.3
-18.4
-9.1
-12.9
-16.1

4h


-16.6
-32.6
-21.1
-9.0
-13.9
-16.9

4i


-16.4
-31.7
-21.5
-8.5
-14.2
-16.6

4. References.

(1) Misra, R.; Kumar, R.; PrabhuRaja, V.; Chandrashekar, T. K. *J. Photochem. Photobiol. A: Chem.* **2005**, *175*, 108.

(2) Halper, S. R.; Cohen, S. M. *Chem. Eur. J.* **2003**, *9*, 4661.

(3) Gryko, D. T.; Zhao, F.; Yasseri, A. A.; Roth, K. M.; Bocian, D. F.; Kuhr, W. G.; Lindsey, J. S. *J. Org. Chem.* **2000**, *65*, 7356.

(4) Littler, B. J.; Miller, M. A.; Hung, C. H.; Wagner, R. W.; Oshea, D. F.; Boyle, P. D.; Lindsey, J. S. *J. Org. Chem.* **1999**, *64*, 1391.

(5) Venkatraman, S.; Kumar, R.; Sankar, J.; Chandrashekar, T. K.; Sendhil, K.; Vijyan, C.; Kelling, A.; Senge, M. O. *Chem. Eur. J.* **2004**, *10*, 1423.

(6) Kumar, R.; Misra, R.; PrabhuRaja, V.; Chandrashekar, T K. *Chem. Eur. J.* **2005**, *11*, 5695.

(7) Misra, R.; Kumar, R.; Chandrashekar, T. K.; Nag, A.; Goswami, D. *Org. Lett.* **2006**, *8*, 629.

(8) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.

(9) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(10) Gaussian 03, Revision C.02, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; yengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.;

Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A., version Gaussian 03, Revision C.02; Gaussian, Inc.: Wallingford CT, 2004.

(11) Hariharan, P. C.; Pople, J. A. *Chem. Phys. Lett.* **1972**, *16*, 217.

(12) Hay, P. J.; Wadt, W. R. J. Chem. Phys. **1985**, 82, 299.

(13) Hay, P. J.; Wadt, W. R. J. Chem. Phys. **1985**, 82, 270.

(14) Wadt, W. R.; Hay, P. J. J. Chem. Phys. **1985**, 82, 284.

(15) Politzer, P.; Truhlar, D. G., Chemical Applications of Atomic and Molecular Electrostatic Potentials. Plenum: New York, 1981.

(16) Gadre, S. R.; Shirsat, R. N., Electrostatics of Atoms and Molecules. Universities Press: Hyderabad, 2000.

(17) Murray, J. S.; Ranganathan, S.; Politzer, P. *J. Org. Chem.* **1991,** *56*, 3734.

(18) Luque, F. J.; Orozco, M.; Bhadane, P. K.; Gadre, S. R. *J. Phys. Chem.* **1993,** *97*, 9380.

(19) Bagdassarian, C. K.; Schramm, V. L.; Schwartz, S. D. *J. Am. Chem. Soc.* **1996,** *118*, 8825.

(20) Suresh, C. H.; Gadre, S. R. *J. Am. Chem. Soc.* **1998**, *120*, 7049.

(21) Suresh, C. H.; Gadre, S. R. *J. Org. Chem.* **1999,** *64*, 2505.