Supporting Material: (manuscript no. ol0492290)

Purpurinimide-Fullerene Dyads: A Remarkable Effect of the Position of the Fullerene Moiety in the Formation of Atropisomers

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1. Computational Method
2. NMR data

Computational Method:

The structures of compounds 1, 5, 10s are built from the following two major components, fullerene and chlorin. The crystal structure of benzimidazo[2,1-*n*]purpurin-18 13^1-imino-13^2-imide methyl ester (1) was used to build the chlorin moiety of the compounds,1,5,and 10. Appropriate modifications were performed with the SYBYL modeling program version 6.9 (Tripos Inc., St. Louis, MO) using the standard geometry and the SYBYL fragment library. The extended conformation was assumed for n-hexyl tail. The coordinate of fullerene was obtained from the data archive at Computational Chemistry List (2). The geometry of each compound was fully optimized with a semiempirical molecular orbital method, AM1, with the SPARTAN (Wavefunction Inc., Irvine, CA) program. The AM1 optimized fullerene and chlorine moieties are combined by appropriate linker structure by using SYBYL, which are again subjected to the restrained and later unrestrained geometry optimizations by the AM1 method with the SPARTAN program.

Similar to the study by Helaja et al (Ref4a), two diastereomer at C2' position and both atropisomers (alpha nad beta) were examined within the frameof the semi-empirical MO, AM1.

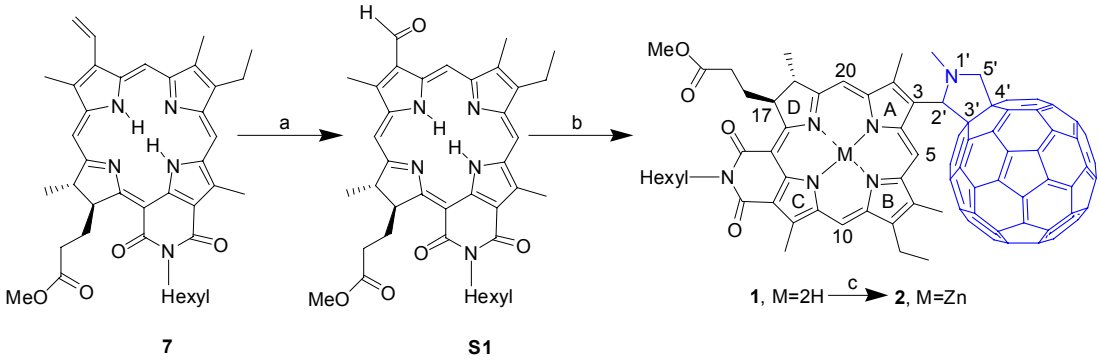
In addition, the azomethine ylides for the 12 position derivative were also examined by the semi-empirical MO, AM1, with the SPARTAN program. The calculation was also performed to obtain the HOMO/LUMO of various ylides. Standard parameters were used to generate the HOMO/LUMO figures. In addition, HOMO/LUMO of unsubstituted fullerene was also obtained by AM1 with the SPARTAN program. It is interesting to note that the nodal pattern of ylide

HOMO is compatible with the fullerene LUMO for the bond along the 6,6 ring junction but not with that of the bond along the 5,6 ring junction.

(1) Kozyrev, A. N.; Suresh, V.; Das, S.; Senge, M. O.; Shibata, M.; Dougherty, T. J.; Pandey, R. K., Tetrahedron 2000, 56, 3353.
http://www.ccl.net/cca/data/fullerenes/c60.cart3d.shtml

Experimental

Melting points are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on Bruker AMX-400 Spectrometer at 400.1 and 100.6 MHz, respectively. Chemical shifts are reported in ppm and referenced to residual solvent resonance peaks ($CDCl_3$: for ^{1}H, 7.26 ppm and ^{13}C, 77.2 ppm). Hydrogen connectivity (C, CH, CH_2, CH_3) information was obtained from DEPT-135 experiments. Proton and carbon peak assignments were based on 2D NMR analysis (COSY, ROESY). UV-vis spectra were recorded on a Varian (Cary-50 Bio) spectrophotometer. CD (Circular Dichroism) spectra were recorded on JASCO J-715 spectrometer. Fluorescence experiment was performed on FluoroMax-2 spectrophotometer (ISA, Inc). Column chromatographic separations were performed over silica gel 60 (70-230 mesh) or neutral alumina (Brockmann grade III, ~150 mesh). Preparative TLC was performed on silica 20 × 20 cm TLC plates (Analtech).



7 S1

Reagents and conditions: (a) $NaIO_4$, OsO_4, H_2O, THF, rt. (b) C_{60}, sarcosine, toluene, reflux. (c) $Zn(OAc)_2 \cdot 2H_2O$, MeOH, $CHCl_3$, rt.

3-Formyl-3-devinyl-purpurin-18-N-hexylimide methyl ester (S1). To a solution of purpurin-18-N-hexylimide methyl ester (**1**, 366 mg, 0.553 mmol) in THF (80 ml) were added a solution of OsO_4 (96 mg, 0.378 mmol) in CCl_4 (20 ml) and a solution of $NaIO_4$ (2.0 g, 9.35 mmol) in water (50 ml) sucessively. The mixture was stirred at rt for 6 h. It was then diluted with CH_2Cl_2 (150

ml), washed with water, and dried with Na_2SO_4. Solvent was removed and the residue was purified with column chromatography on alumina eluting with CH_2Cl_2/EtOAc (v/v 40/1) to provide compound **2** (301 mg, 82%) as dark brown plates. Mp: 169-170 ºC. UV vis in CH_2Cl_2 [λ_{max} (ε)]: 311 (16058), 424 (80795), 494 (4299), 521 (4931), 561 (22506), 672 (7333), 738 (58541). ^{1}H NMR ($CDCl_3$) δ 11.41 (1H, s), 10.15 (1H, s), 9.66 (1H, s), 8.75 (1H, s), 5.43 (1H, dd, *J* = 8.9, 2.3 Hz), 4.46 (2H, t, *J* = 7.7 Hz), 4.40 (1H, q, *J* = 7.2 Hz), 3.86 (3H, s), 3.69 (3H, s), 3.66 (2H, q, *J* = 7.7 Hz), 3.57 (3H, s), 3.23 (3H, s), 2.71 (1H, m), 2.41 (2H, m), 1.99 (3H, m), 1.78 (3H, d, *J* = 7.3 Hz), 1.69 (3H, t, *J* = 7.6 Hz), 1.62 (2H, m), 1.52-1.36 (4H, m), 0.95 (3H, t, *J* = 7.1 Hz), -0.23 (1H, s), -0.41 (1H, s). MS (ESI) *m/z* 664.5 (MH^+, 54), 686.5 (MNa^+, 100). Anal. Calcd for $C_{39}H_{45}N_5O_5$: C, 70.57; H, 6.85; N, 10.55. Found: C, 71.14; H, 6.85; N, 10.53.

Purpurinimide-C60 dyad 1. A mixture of compound **S1** (104 mg, 0.157 mmol) and buckminsterfullerene (C_{60}, 127 mg, 0.176 mmol) and sarcosine (72 mg, 0.808 mmol) in dry toluene (50 ml) was refluxed under N_2 for 17 h. After the reaction mixture was cooled to rt, it was passed through an alumina column with dichloromethane as eluent. The crude product was further purified by column chromatography on alumina eluting with hexanes/CH_2Cl_2 (v/v first 2/3, then 1/2) to give compound **1** (67 mg, 30%) and unreacted compound **S1** (25 mg). Data of compound **1**: Dark brown plates. Mp: >300 ºC. UV vis in $CHCl_3$ [λ_{max} (ε)]: 370 (59638), 421 (149136), 485 (7979), 514 (8802), 551 (25911), 655 (8637), 711 (57417). This compound is a mixture of four isomers with a ratio of 1:1:0.6:0.6 based on ^{1}H NMR spectrum. ^{1}H NMR ($CDCl_3$) δ 11.05, 11.03, 9.54, 9.53 (1H, s, 5-H), 9.65, 9.61 (1H, s, 10-H), 8.69, 8.65, 8.57, 8.54 (1H, s, 20-H), 6.423, 6.415, 5.99, 5.88 (1H, s, 2'-H), 5.40 (1H, m, 17-H), 4.92, 4.82, 4.26, 3.98 (2H, doublets or overlapping doublets, 5'-H), 4.56-4.30 (3H, m, 18-H and -N*CH*$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 3.84, 3.81, 3.79, 3.77 (3H, s, 12-CH_3), 3.81, 3.73, 3.37, 3.30 (3H, s, 2-CH_3), 3.66 (2H, m, 8-*CH*$_2$CH$_3$), 3.61, 3.55, 3.52 (3H, s, -COOCH_3), 3.25, 3.24, 3.04, 3.01 (3H, s, 7-CH_3), 2.82, 2.72, 2.58, 2.54 (3H, s, 1'-CH_3), 2.74, 2.44, 1.99 (1H, 2H, 3H, 17-*CH*$_2$*CH*$_2$COOCH_3 and -NCH$_2$*CH*$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 1.88-1.56 (8H, m, 18-CH_3, 8-CH$_2$*CH*$_3$, -NCH$_2$CH$_2$*CH*$_2$CH$_2$CH$_2$CH$_3$), 1.45 (4H, m, -NCH$_2$CH$_2$CH$_2$*CH*$_2$*CH*$_2$CH$_3$), 0.95 (3H, t, *J* = 7.1 Hz, -NCH$_2$CH$_2$CH$_2$CH$_2$CH$_2$*CH*$_3$), -0.09--0.22 (2H, overlapping s, 2 × -*NH*). ^{13}C NMR ($CDCl_3$) δ 176.92, 176.88, 176.75, 174.84, 174.64, 174.12, 174.00, 173.90, 167.58, 167.54, 167.48, 163.49, 163.44, 163.40, 163.37, 156.63, 156.58, 155.96, 155.09, 154.99, 154.86, 154.76, 153.82, 153.77,

153.64, 153.56, 153.49, 153.43, 153.37, 153.06, 153.02, 152.74, 150.82, 150.54, 147.4-134.6 (very complex signals), 134.12, 133.92, 133.86, 133.76, 132.58, 132.44, 116.68, 108.31, 108.24, 107.07, 106.98, 103.43, 103.28, 98.13, 98.04, 97.81, 97.77, 95.16, 94.92, 78.57, 78.52, 78.21, 78.12, 77.85, 77.42, 70.62, 70.42, 69.80, 69.57, 69.52, 55.11, 51.72, 51.66, 49.55, 49.31, 49.13, 40.65, 40.60, 40.42, 40.27, 40.16, 32.83, 32.01, 31.79, 29.91, 29.65, 29.25, 27.41, 24.39, 24.33, 24.14, 24.07, 22.96, 19.69, 19.66, 17.84, 14.36, 13.10, 12.98, 12.75, 12.68, 12.24, 12.19, 11.56, 11.18, 11.10. MS (FAB) *m/z* 690.4 (100), 1411.4 (MH^+, 4). HRMS (FAB): Calcd for $C_{101}H_{51}N_6O_4$ (M+H), 1411.3970; Found 1411.3930. Anal. Calcd for $C_{101}H_{50}N_6O_4$: C, 85.94; H, 3.57; N, 5.95. Found: C, 85.81; H, 3.87; N, 5.85.

Zn-purpurinimide-C60 dyad 2. To a solution of the compound **1** (42 mg) in $CHCl_3$ (50 ml) was added a solution of $Zn(OAc)_2{\cdot}2H_2O$ (500 mg) in MeOH (15 ml). The resultant solution was degassed with vacuum and N_2, and it was stirred under N_2 at rt for 19 hours. The reaction mixture was washed with water (6 × 50 ml), dried with Na_2SO_4, and filtered. Solvent was removed to provide compound **2** as dark brown plates in quantitative yield. Mp: >300 ºC. UV vis in $CHCl_3$ [λ_{max} (ε)]: 404 (71468), 427 (120372), 515 (6745), 555 (11082), 631 (12688), 685 (57094). ^{1}H NMR ($CDCl_3$) δ 11.04, 11.01, 9.42, 9.39, 8.42, 8.41, 8.31, 8.30 (3H, s, 5-H, 10-H, 20-H), 6.41, 6.02, 5.98 (1H, s, 2'-H), 5.32-5.02, 4.48-3.90 (6H, m, 17-H, 18-H, 5'-H, -N*CH*$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 3.73, 3.49, 3.48, 3.44, 3.31, 3.27, 3.24, 3.14, 3.03, 2.98, 2.95, 2.83 (15H, s, 2-CH_3, 7-CH_3, 12-CH_3, 1'-CH_3, -$COOCH_3$), 3.62 (2H, m, 8-*CH*$_2$CH$_3$), 2.74-1.92 (4H, 17-*CH*$_2$*CH*$_2$$COOCH_3$), 1.88-1.52 (8H, m, 18-$CH_3$, 8-$CH_2$*CH*$_3$, -$NCH_2$*CH*$_2$$CH_2CH_2CH_2CH_3$), 1.44 (2H, m, -$NCH_2CH_2$*CH*$_2$$CH_2CH_2CH_3$), 1.33 (4H, m, -$NCH_2CH_2CH_2$*CH*$_2$*CH*$_2$$CH_3$), 0.89 (3H, m, -$NCH_2CH_2CH_2CH_2CH_2$*CH*$_3$). MS (FAB) *m/z* 752.4 (100), 1475.4 (MH^+, 62). Anal. Calcd for $C_{101}H_{48}N_6O_4Zn{\cdot}4H_2O$: C, 78.42; H, 3.65; N, 5.43. Found: C, 78.59; H, 3.77; N, 5.33.

8-Formyl-8-deethyl-meso-purpurin-18-N-hexylimide methyl ester 4. Followed the procedure described for the preparation of compound **S1**, compound **4** was obtained as dark brown plates in 77% yield from compound **3**. Data of compound **4**: Mp: 210-203 ºC. UV vis in CH_2Cl_2 [λ_{max} (ε)]: 321 (25603), 348 (24899), 372 (24076), 417 (50149), 440 (211520), 523 (11979), 558 (7047), 626 (5285), 681 (39227). ^{1}H NMR ($CDCl_3$) δ 10.82 (1H, s), 10.16 (1H, s), 8.97 (1H, s), 8.47 (1H, s), 5.36 (1H, dd, *J* = 8.9, 2.2 Hz), 4.44 (2H, t, *J* = 7.7 Hz), 4.32 (1H, q, *J* = 7.6 Hz), 3.67 (2H, q, *J* = 7.7 Hz), 3.62 (3H, s), 3.60 (3H, s), 3.28 (3H, s), 3.22 (3H, s), 2.73 (1H, m), 2.44

(2H, m), 1.98 (3H, m), 1.80 (3H, d, J = 7.2 Hz), 1.67 (3H, t, J = 7.6 Hz), 1.62 (2H, m), 1.55-1.36 (4H, m), 0.96 (3H, t, J = 7.0 Hz), -0.18 (1H, s), -0.23 (1H, s). MS (ESI) *m/z* 663.8 (M^+, 100). ^{13}C NMR ($CDCl_3$) δ 186.9 (CH), 178.8 (C), 176.2 (C), 173.9 (C), 167.2 (C), 162.8 (C), 150.1 (C), 148.7 (C), 146.3 (C), 144.6 (C), 144.0 (C), 143.7 (C), 139.6 (C), 135.6 (C), 134.0 (C), 132.9 (C), 131.1 (C), 116.9 (C), 111.3 (CH), 102.4 (CH), 97.4 (C), 95.0 (CH), 55.2 (CH), 51.7 (CH_3), 49.1 (CH), 40.6 (CH_2), 32.7 (CH_2), 31.9 (CH_2), 31.8 (CH_2), 29.2 (CH_2), 27.4 (CH_2), 24.2 (CH_3), 23.0 (CH_2), 19.3 (CH_2), 17.0 (CH_3), 14.3 (CH_3), 12.5 (CH_3), 10.9 (CH_3), 10.8 (CH_3).

Purpurinimide-C60 dyad 5. Followed the procedure described for the preparation of compound **1**, compound **5** (102 mg, 34%) was obtained by reacting compound **4** (140 mg, 0.211 mmol) with C60 (183 mg, 0.254 mmol) and sarcosine (94 mg, 1.055 mmol) in dry toluene (30 ml). Unreacted compound **4** (39 mg) was recovered. Data of **5**: Dark brown plates. Mp: >300 ºC. UV vis in $CHCl_3$ [λ_{max} (ε)]: 312 (60216), 342 (60118), 426 (202838), 512 (12903), 548 (18280), 639 (8602), 693 (55133). This compound is a mixture of four isomers with a ratio of 1:1:0.3:0.3 based on ^1H NMR spectrum. ^1H NMR ($CDCl_3$) δ 11.58, 11.56, 9.94, 9.89 (1H, s, 10-H), 9.31, 9.30, 9.21, 9.19 (1H, s, 5-H), 8.50, 8.47, 8.45 (1H, s, 20-H), 6.40, 6.31, 5.91, 5.87 (1H, s, 2'-H), 5.36, 5.31 (1H, br d, J = 8.8 Hz, 17-H), 4.99, 4.91, 4.82, 4.27, 4.16, 4.13 (2H, doublets or overlapping doublets, 5'-H), 4.47 (2H, m, -N*CH*$_2$$CH_2CH_2CH_2CH_3$), 4.31 (1H, m, 18-H), 3.94, 3.68 (3H, s, 12-CH_3), 3.75, 3.71, 3.30, 3.23 (3H, s, 7-CH_3), 3.70 (2H, m, 3-*CH*$_2$$CH_3$), 3.61, 3.58, 3.57, 3.55 (3H, s, -$COOCH_3$), 3.20, 3.19 (3H, s, 2-CH_3), 2.90, 2.81, 2.78, 2.74 (3H, s, 1'-CH_3), 2.71, 2.43, 1.99 (1H, 2H, 3H, 17-*CH*$_2$*CH*$_2$$COOCH_3$ and -NCH_2*CH*$_2$$CH_2CH_2CH_2CH_3$), 1.75 (3H, overlapping doublets, 18-CH_3), 1.69 (3H, t, J = 7.7 Hz, 3-CH_2*CH*$_3$), 1.62 (2H, m, -NCH_2CH_2*CH*$_2$$CH_2CH_2CH_3$), 1.45 (4H, m, -$NCH_2CH_2CH_2$*CH*$_2$*CH*$_2$$CH_3$), 0.95 (3H, m, -$NCH_2CH_2CH_2CH_2CH_2$*CH*$_3$), 0.16, 0.14, 0.10, 0.15, -0.01, -0.04, -0.09, -0.03 (2H, s, 2 × -*NH*). ^{13}C NMR ($CDCl_3$) δ 177.48, 177.41, 177.31, 176.03, 175.85, 175.62, 175.52, 173.96, 173.89, 167.48, 167.41, 163.52, 163.46, 156.99, 156.96, 156.35, 156.28, 155.28, 154.31, 154.28, 153.99, 153.86, 153.77, 153.64, 153.13, 149.42, 149.32, 148.34, 148.31, 146.91, 146.56-135.40 (very complex signals), 131.75, 131.68, 131.48, 131.42, 130.98, 116.31, 116.28, 116.20, 116.14, 113.98, 108.96, 102.26, 102.22, 101.82, 97.89, 97.77, 97.58, 97.49, 94.81, 94.71, 94.58, 94.54, 78.82, 78.23, 78.19, 78.05, 70.60, 70.46, 70.38, 69.83, 69.47, 69.42, 54.96, 54.90, 51.69, 51.64, 49.47, 49.28, 49.22, 40.54, 40.37, 40.29, 32.77, 32.66, 31.97, 31.83, 31.56, 29.20, 27.38, 24.21,

24.10, 23.96, 22.92, 19.43, 17.10, 14.34, 13.01, 12.35, 12.30, 12.22, 11.00. MS (FAB) *m/z* 690.2 (100), 1411.0 (MH^+, 20). HRMS (FAB): Calcd for $C_{101}H_{51}N_6O_4$ (M+H), 1411.3970; Found 1411.3980. Anal. Calcd for $C_{101}H_{50}N_6O_4 \cdot 1/2H_2O$: C, 85.40; H, 3.62; N, 5.92. Found: C, 85.13; H, 4.02; N, 5.87.

Zn-purpurinimide-C60 dyad 6. Followed the procedure described for the preparation of compound **2**, compound **6** was obtained as dark brown plates in quantitative yield from compound **5**. Data of **6**: Mp: >300 ºC. UV vis in $CHCl_3$ [λ_{max} (ε)]: 313 (55593), 431 (133991), 513 (8509), 552 (8169), 618 (11913), 666 (45609). This compound is a mixture of four isomers with a ratio of 1:1:0.4:0.4 based on ^{1}H NMR spectrum. ^{1}H NMR ($CDCl_3$) δ 11.20, 11.18, 9.62, 9.59, 9.09, 8.99, 8.26, 8.21, 8.19, 8.17 (3H, s, H-5, H-10, H-20), 8.39, 8.36, 5.98 (1H, s, 2'-H), 5.26-4.92, 4.46-3.80 (6H, m, 17-H, 18-H, 5'-H, -N*CH*$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 3.72, 3.70, 3.65, 3.52, 3.36, 3.28, 3.11, 3.08, 3.06, 3.03, 2.99, 2.94, 2.92, 2.89 (15H, s, 2-CH_3, 7-CH_3, 12-CH_3, 1'-CH_3, -$COOCH_3$), 3.59 (2H, m, 3-*CH*$_2$CH$_3$), 2.40-1.12 (18H, m, 8-CH$_2$*CH*$_3$, 17-*CH*$_2$*CH*$_2$COOCH$_3$, 18-CH_3, -NCH$_2$*CH*$_2$*CH*$_2$*CH*$_2$*CH*$_2$CH$_3$), 0.88 (3H, m, -NCH$_2$CH$_2$CH$_2$CH$_2$CH$_2$*CH*$_3$). MS (FAB) *m/z* 752.4 (100), 1474.4 (M^+, 82).

12-Hydroxymethyl-12-demethyl-purpurin-18-N-hexylimide methyl ester (8) and 12-formyl-12-demethyl-purpurin-18-N-hexylimide methyl ester (9). To a solution of compound **7** (458 mg) in a mixture of THF (45 ml) and MeOH (30 ml) was added a solution of $LiOH \cdot H_2O$ (600 mg) in water (30 ml). With exposure to air, the mixture was stirred under dark (covered with aluminum foil) at rt for 21 h. After addition of aqueous acetic acid (1%, 100 ml), the mixture was extracted with CH_2Cl_2. The CH_2Cl_2 layer was washed with water, dried over Na_2SO_4, and filtered. The filtrate was then treated with excess CH_2N_2 (made from 1.0 g of Diazald®). Solvent was removed, and the residua was purified with column chromatography on silica gel eluting with 3% acetone/CH_2Cl_2 to provide compounds **8** (152 mg, 33%) and **9** (124 mg, 26%).

Converting compound 8 to compound 9. To a solution of compound **8** (129 mg, 0.190 mmol) in dry CH_2Cl_2 (50 ml) were added TPAP (20 mg) and NMO (138 mg). The mixture was stirred at rt for 3 h. It was filtered, and solvent was removed. The resultant residua were purified by column chromatography on silica gel eluting with 3% acetone/CH_2Cl_2 to give compound **9** (84 mg, 65%) as dark brown plates.

Purpurinimide-C60 dyads 10a and 10b. A mixture of compound **9** (163 mg, 0.241 mmol) and buckminsterfullerene (C60, 174 mg, 0.242 mmol) and sarcosine (108 mg, 1.212 mmol) in dry

toluene (80 ml) was refluxed under N_2 for 20 h. After the reaction mixture was cooled to rt, it was passed through an alumina column with dichloromethane as eluant. The fast moving fraction was collected and concentrated to a volume of around 10 ml. CH_2Cl_2 was added, and the mixture was refrigerated for 3 h. It was then filtered, and the solid was washed with CH_2Cl_2. The filtrate was evaporated to dryness. The residua was dissolved in CH_2Cl_2 (30 ml), and refrigerated. The solid was filtered and washed with CH_2Cl_2. The two crops of solid compound were combined and dried under high vacuum to give pure compound **10a** (45 mg, 13%). The filtrate was further purified by preparative silica TLC using MeOH/CH_2Cl_2 (0.8%) as developing solvent to give compound **10b** (48 mg, 14%). Data of compound **10a**: Brown powder. Mp: >300 ºC. UV vis in $CHCl_3$ [λ_{max} (ε)]: 372 (55271), 424 (88524), 561 (20221), 655 (10874), 713 (49070). ^{1}H NMR (CS_2/$CDCl_3$ = 2/1) δ 11.62 (1H, s, 10-H), 9.18 (1H, s, 5-H), 8.44 (1H, s, 20-H), 7.87 (1H, dd, *J* = 18.0, 11.6 Hz, 3^1-H), 7.67 (1H, s, 2'-H), 6.29 (1H, d, *J* = 17.8 Hz, 3^{2b}-H), 6.17 (1H, d, *J* = 11.7 Hz, 3^{2a}-H), 5.36 (1H, d, *J* = 9.5 Hz, part of AB system, one of protons of 5'-H), 5.20 (1H, dd, *J* = 9.1, 2.2 Hz, 17-H), 4.73 (1H, d, *J* = 9.8 Hz, part of AB system, one of protons of 5'-H), 4.35 (2H, t, *J* = 7.7 Hz, -N*CH*$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 4.30 (1H, q, *J* = 7.5 Hz, 18-H), 3.77 (2H, m, 8-*CH*$_2$CH$_3$), 3.57 (3H, s, -COOCH$_3$), 3.33 (3H, s, 2-CH$_3$), 3.16 (3H, s, 7-CH$_3$), 3.07 (3H, s, 1'-CH$_3$), 2.75, 2.53, 2.41, 1.87 (1H, 2H, 1H, m, 17-*CH*$_2$*CH*$_2$COOCH$_3$), 1.85 (3H, t, *J* = 7.6 Hz, 8-CH$_2$*CH*$_3$), 1.81 (2H, m, -NCH$_2$*CH*$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 1.73 (3H, d, *J* = 7.3 Hz, 18-CH$_3$), 1.50 (2H, m, -NCH$_2$CH$_2$*CH*$_2$CH$_2$CH$_2$CH$_3$), 1.38 (4H, m, -NCH$_2$CH$_2$CH$_2$*CH*$_2$*CH*$_2$CH$_3$), 0.93 (3H, t, *J* = 7.0 Hz, -NCH$_2$CH$_2$CH$_2$CH$_2$CH$_2$*CH*$_3$), 0.57 (1H, s, -NH), 0.39 (1H, s, -NH). MS (FAB) *m/z* 702.4 (100), 1423.3 (MH^+, 0.5). HRMS (FAB): Calcd for $C_{102}H_{51}N_6O_4$ (M+H), 1423.3970; Found 1423.3930. Anal. Calcd for $C_{102}H_{50}N_6O_4 \cdot 4H_2O$: C, 81.91; H, 3.91; N, 5.62. Found: C, 81.88; H, 4.25; N, 5.24. Data of **10b**: Brown powder. Mp: >300 ºC. UV vis in $CHCl_3$ [λ_{max} (ε)]: 369 (55556), 424 (89558), 562 (20134), 655 (10610), 714 (49290). ^{1}H NMR (CS_2/$CDCl_3$ = 2/1) δ 11.63 (1H, s, 10-H), 9.18 (1H, s, 5-H), 8.44 (1H, s, 20-H), 7.86 (1H, dd, *J* = 18.0, 11.6 Hz, 3^1-H), 7.71 (1H, s, 2'-H), 6.29 (1H, d, *J* = 17.9 Hz, 3^{2b}-H), 6.17 (1H, d, *J* = 11.5 Hz, 3^{2a}-H), 5.35 (1H, d, *J* = 9.6 Hz, part of AB system, one of protons of 5'-H), 5.29 (1H, br d, *J* = 8.8 Hz, 17-H), 4.75 (1H, d, *J* = 9.7 Hz, part of AB system, one of protons of 5'-H), 4.36 (2H, m, -N*CH*$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 4.29 (1H, q, *J* = 7.6 Hz, 18-H), 3.77 (2H, q, *J* = 7.6 Hz, 8-*CH*$_2$CH$_3$), 3.60 (3H, s, -COOCH$_3$), 3.33 (3H, s, 2-CH$_3$), 3.20 (3H, s, 7-CH$_3$), 3.16 (3H, s, 1'-CH$_3$), 2.70, 2.40, 1.94 (1H, 2H, 1H, m, 17-*CH*$_2$*CH*$_2$COOCH$_3$), 1.85 (3H, t, *J* = 7.6 Hz, 8-

CH_2CH_3), 1.81 (2H, m, -$NCH_2CH_2CH_2CH_2CH_2CH_3$), 1.71 (3H, d, J = 7.4 Hz, 18-CH_3), 1.49 (2H, m, -$NCH_2CH_2CH_2CH_2CH_2CH_3$), 1.38 (4H, m, -$NCH_2CH_2CH_2CH_2CH_2CH_3$), 0.93 (3H, t, J = 7.0 Hz, -$NCH_2CH_2CH_2CH_2CH_2CH_3$), 0.56 (1H, s, -NH), 0.38 (1H, s, -NH). ^{1}H NMR ($CDCl_3$) δ 11.60 (1H, s, 10-H), 9.20 (1H, s, 5-H), 8.40 (1H, s, 20-H), 7.80 (1H, dd, J = 18.0, 11.6 Hz, 3^1-H), 7.63 (1H, s, 2'-H), 6.23 (1H, d, J = 18.0 Hz, 3^{2b}-H), 6.12 (1H, d, J = 11.5 Hz, 3^{2a}-H), 5.35 (1H, dd, J = 8.9, 1.9 Hz, 17-H), 5.15 (1H, d, J = 9.7 Hz, part of AB system, one of protons of 5'-H), 4.55 (1H, d, J = 9.8 Hz, part of AB system, one of protons of 5'-H), 4.39 (2H, m, -$NCH_2CH_2CH_2CH_2CH_2CH_3$), 4.27 (1H, q, J = 7.2 Hz, 18-H), 3.73 (2H, m, 8-CH_2CH_3), 3.58 (3H, s, -$COOCH_3$), 3.25 (3H, s, 2-CH_3), 3.13 (3H, s, 7-CH_3), 2.96 (3H, s, 1'-CH_3), 2.68, 2.37, 2.00 (1H, 2H, 1H, m, 17-$CH_2CH_2COOCH_3$), 1.81 (2H, m, -$NCH_2CH_2CH_2CH_2CH_2CH_3$), 1.75 (3H, t, J = 7.6 Hz, 8-CH_2CH_3), 1.67 (3H, d, J = 7.4 Hz, 18-CH_3), 1.49 (2H, m, -$NCH_2CH_2CH_2CH_2CH_2CH_3$), 1.36 (4H, m, -$NCH_2CH_2CH_2CH_2CH_2CH_3$), 0.89 (3H, t, J = 7.1 Hz, -$NCH_2CH_2CH_2CH_2CH_2CH_3$), 0.69 (1H, s, -NH), 0.48 (1H, s, -NH). ^{13}C NMR ($CDCl_3$) δ 177.21, 176.99, 173.96, 167.32, 163.04, 157.91, 157.39, 155.49, 154.21, 153.65, 150.51, 147.45, 147.21, 146.75, 146.32, 146.23, 146.09, 146.00, 145.91, 145.88, 145.85, 145.82, 145.78, 145.70, 145.64, 145.56, 145.48, 145.33, 145.04, 144.92, 144.55, 144.51, 144.30, 144.00, 143.21, 142.84, 142.68, 142.52, 142.39, 142.33, 142.19, 142.10, 142.06, 142.01, 141.89, 141.56, 141.49, 141.20, 141.16, 140.28, 140.20, 140.01, 139.21, 137.84, 137.57, 137.08, 136.59, 136.46, 136.24, 135.17, 134.39, 132.27, 130.96, 128.59, 123.56, 116.78, 113.58, 102.01, 98.49, 94.75, 78.51, 70.75, 70.18, 54.51, 51.69, 49.72, 40.70, 40.60, 32.66, 32.00, 31.63, 29.89, 29.01, 27.16, 23.94, 22.85, 19.89, 17.43, 14.39, 12.04, 11.25. MS (FAB) *m/z* 702.4 (100), 1423.4 (MH^+, 8). HRMS (FAB): Calcd for $C_{102}H_{51}N_6O_4$ (M+H), 1423.3970; Found 1423.3900. Anal. Calcd for $C_{102}H_{50}N_6O_4 \cdot 1/2H_2O$: C, 85.52; H, 3.59; N, 5.87. Found: C, 85.46; H, 4.14; N, 5.71.

Zn-purpurinimide-C60 dyad 11a. Compound **10a** (32 mg) was dissolved in CS_2 (20 ml), the solution was then diluted with $CHCl_3$ (150 ml, washed with 5% $NaHCO_3$ before use). A solution of $Zn(OAc)_2 \cdot 2H_2O$ (2.0 g) in MeOH (70 ml) was added to above solution. The mixture was degassed with vacuum and N_2, and stirred at rt under N_2 for 66 h. TLC analysis showed the reaction was complete. The reaction mixture was washed with water, dried over Na_2SO_4, and filtered. The filtrate was concentrated to a volume of about 10 ml. It was passed though a silica column eluting with acetone/CH_2Cl_2 (2%) to provide compound **11a** (31 mg, 93%) as dark green powder. Mp: >300 ºC. UV vis in $CHCl_3$ [λ_{max} (ε)]: 409 (61562), 431 (69741), 563 (10785), 640

(12762), 695 (55990). ^{1}H NMR (CS_2/$CDCl_3$ = 2/1) δ 11.55 (1H, s, 10-H), 9.07 (1H, s, 5-H), 8.31 (1H, s, 20-H), 7.81 (1H, dd, *J* = 17.8, 11.6 Hz, 3^1-H), 7.56 (1H, s, 2'-H), 6.11 (1H, d, *J* = 17.9 Hz, 3^{2b}-H), 6.03 (1H, d, *J* = 11.5 Hz, 3^{2a}-H), 5.31 (1H, d, *J* = 9.7 Hz, part of AB system, one of protons of 5'-H), 5.11 (1H, br d, *J* = 8.6 Hz, 17-H), 4.67 (1H, d, *J* = 9.5 Hz, part of AB system, one of protons of 5'-H), 4.24 (2H, t, *J* = 7.5 Hz, -N*CH*$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 4.07 (1H, q, *J* = 7.2 Hz, 18-H), 3.78 (2H, q, *J* = 7.7 Hz, 8-*CH*$_2$CH$_3$), 3.26, 3.17, 3.09, 3.05 (each 3H, s, 2-CH_3, 7-CH_3, 1'-CH_3, -$COOCH_3$), 2.37, 2.07, 1.72 (1H, 2H, 3H, m, 17-*CH*$_2$*CH*$_2$$COOCH_3$, -NCH$_2$*CH*$_2CH_2CH_2CH_2CH_3$), 1.82 (3H, t, *J* = 7.6 Hz, 8-CH$_2$*CH*$_3$), 1.64 (3H, d, *J* = 7.2 Hz, 18-CH_3), 1.44 (2H, m, -NCH$_2$CH$_2$*CH*$_2$CH$_2$CH$_2$CH$_3$), 1.35 (4H, m, -NCH$_2$CH$_2$CH$_2$*CH*$_2$*CH*$_2$CH$_3$), 0.90 (3H, t, *J* = 6.7 Hz, -NCH$_2$CH$_2$CH$_2$CH$_2$CH$_2$*CH*$_3$). MS (FAB) *m/z* 764.4 (100), 1487.4 (MH^+, 51). Anal. Calcd for $C_{102}H_{48}N_6O_4Zn·3/2H_2O$: C, 79.04; H, 3.58; N, 5.42. Found: C, 78.92; H, 3.57; N, 5.35.

Zn-purpurinimide-C60 dyad 11b. To a solution of compound **10b** (35 mg) in $CHCl_3$ (60 ml, washed with 5% $NaHCO_3$ before use) was added a solution of $Zn(OAc)_2·2H_2O$ (1.0 g) in MeOH (30 ml) was added to above solution. The mixture was degassed with vacuum and N_2, and stirred at rt under N_2 for 24 h. TLC analysis showed the reaction was complete. The reaction mixture was washed with water, dried over Na_2SO_4, and filtered. Solvent was removed to give compound **11b** (36 mg, 98%) as dark green powder. Mp: >300 ºC. UV vis in $CHCl_3$ [λ_{max} (ε)]: 409 (60735), 431 (69674), 564 (10192), 641 (12866), 695 (56809). ^{1}H NMR (CS_2/$CDCl_3$ = 2/1) δ 11.60 (1H, s, 10-H), 9.10 (1H, s, 5-H), 8.29 (1H, s, 20-H), 7.81 (1H, dd, *J* = 17.5, 11.3 Hz, 3^1-H), 7.64 (1H, s, 2'-H), 6.12 (1H, d, *J* = 18.1 Hz, 3^{2b}-H), 6.05 (1H, d, *J* = 11.6 Hz, 3^{2a}-H), 5.37 (1H, d, *J* = 9.5 Hz, part of AB system, one of protons of 5'-H), 5.30 (1H, br d, *J* = 8.6 Hz, 17-H), 4.73 (1H, d, *J* = 9.5 Hz, part of AB system, one of protons of 5'-H), 4.29 (2H, m, -N*CH*$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 4.18 (1H, q, *J* = 7.1 Hz, 18-H), 3.80 (2H, m, 8-*CH*$_2$CH$_3$), 3.53 (3H, s, -$COOCH_3$), 3.21, 3.20, 3.19 (each 3H, s, 2-CH_3, 7-CH_3, 1'-CH_3), 2.65, 2.41, 2.27, 1.96 (each 1H, m, 17-*CH*$_2$*CH*$_2$$COOCH_3$), 1.85 (3H, t, *J* = 7.3 Hz, 8-CH$_2$*CH*$_3$), 1.77 (2H, m, -NCH$_2$*CH*$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 1.66 (3H, d, *J* = 7.2 Hz, 18-CH_3), 1.46 (2H, m, -NCH$_2$CH$_2$*CH*$_2$CH$_2$CH$_2$CH$_3$), 1.37 (4H, m, -NCH$_2$CH$_2$CH$_2$*CH*$_2$*CH*$_2$CH$_3$), 0.92 (3H, t, *J* = 7.0 Hz, -NCH$_2$CH$_2$CH$_2$CH$_2$CH$_2$*CH*$_3$). MS (FAB) *m/z* 764.4 (100), 1486.4 (M^+, 2). Anal. Calcd for $C_{102}H_{48}N_6O_4Zn·H_2O$: C, 81.41; H, 3.35; N, 5.58. Found: C, 81.60; H, 3.45; N, 5.54.

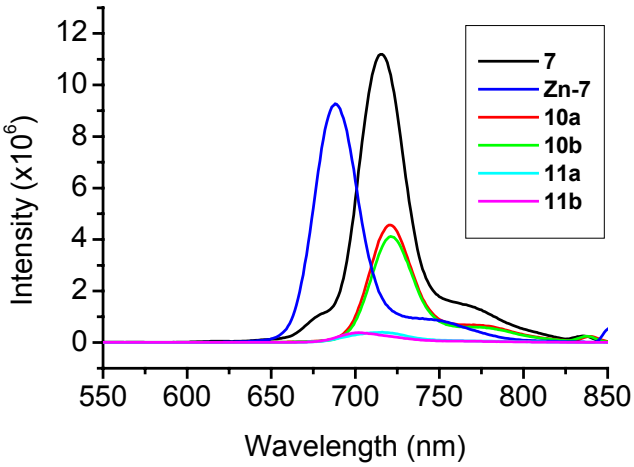


Figure S1. Fluorescence spectra of dyads **10a**, **10b**, **11a**, **11b** and chlorins **7**, **Zn-7**. (Concentration: 1.0 μM in $CHCl_3$. Excited at the corresponding Soret band. For **7**, 416 nm; **Zn-7**, 425 nm; **10a**, 424 nm; **10b**, 424 nm; **11a**, 431 nm; **11b**, 431 nm.)

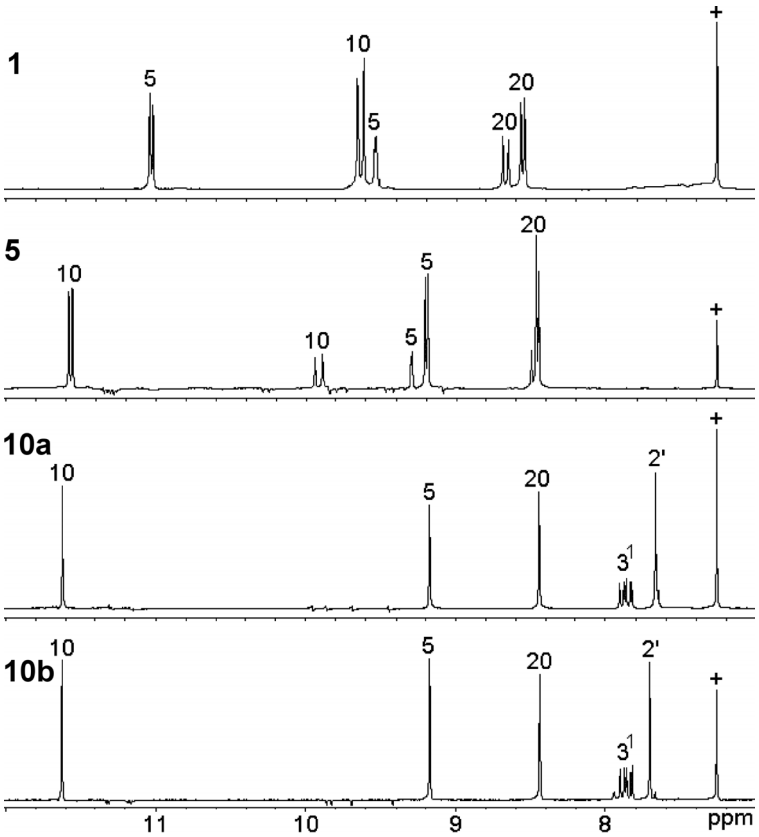


Figure S2. Partial ^{1}H NMR spectra of dyads **1**, **5**, **10a**, **10b**.
(The signals labeled with + are the resonances of residual $CHCl_3$ in $CDCl_3$.)

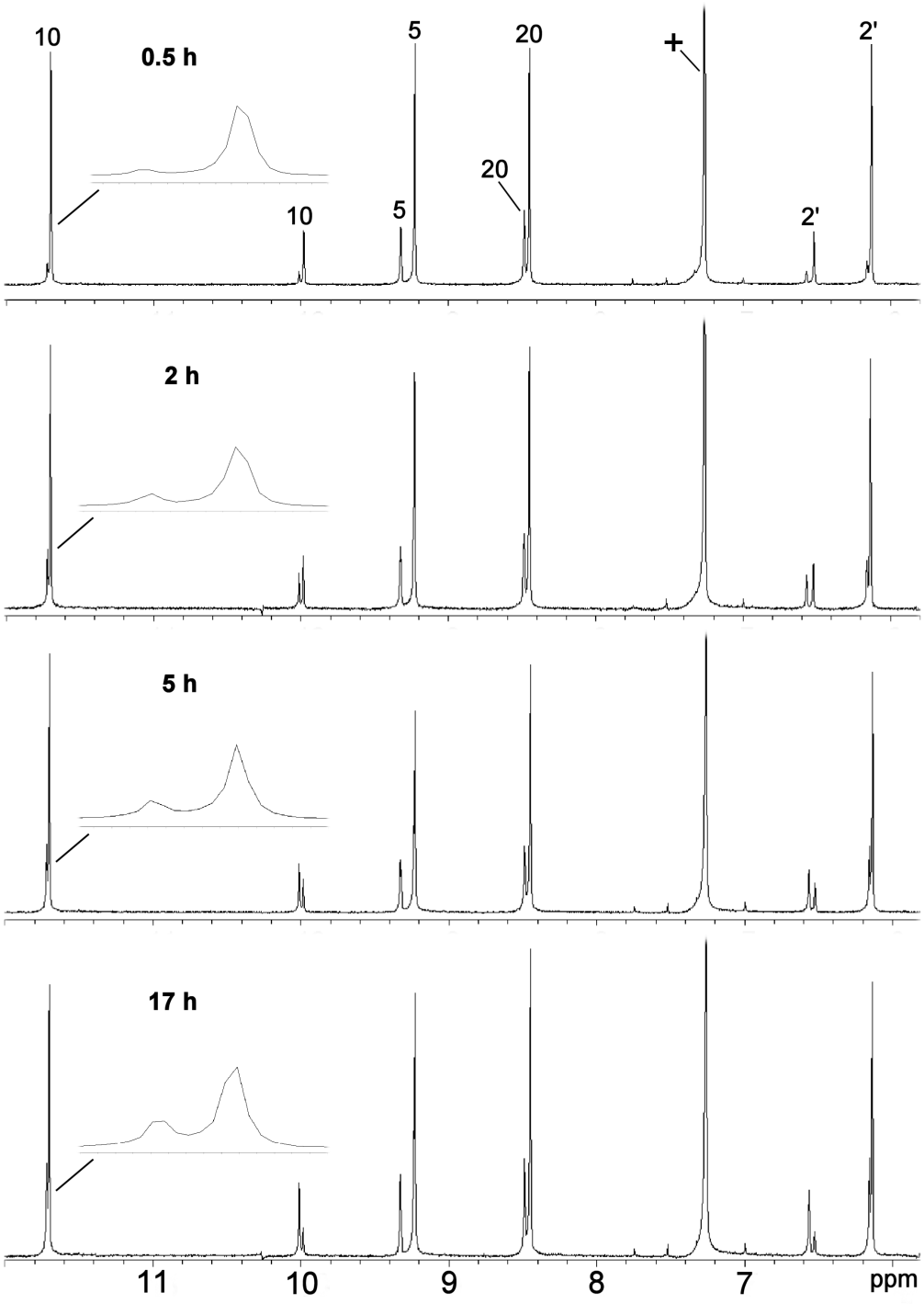


Figure S3. ^{1}H NMR spectral study of the atropisomerism of the fast-moving isomers of dyad **5** at different time point. (The same study for the slow-moving isomers is very similar to the fast-moving one, and overlapping the 17 h spectra of the fast-moving and slow-moving isomers gives the spectrum of dyad **5** as shown in Figure 2.) (The signals labeled with + are the resonances of residual $CHCl_3$ in $CDCl_3$; All NMR spectra were measured at room temperature, i.e. 20 ºC.)