Supporting Information (SI)

High-Efficiency Cycloruthenated Sensitizers for Dye-Sensitized Solar Cells

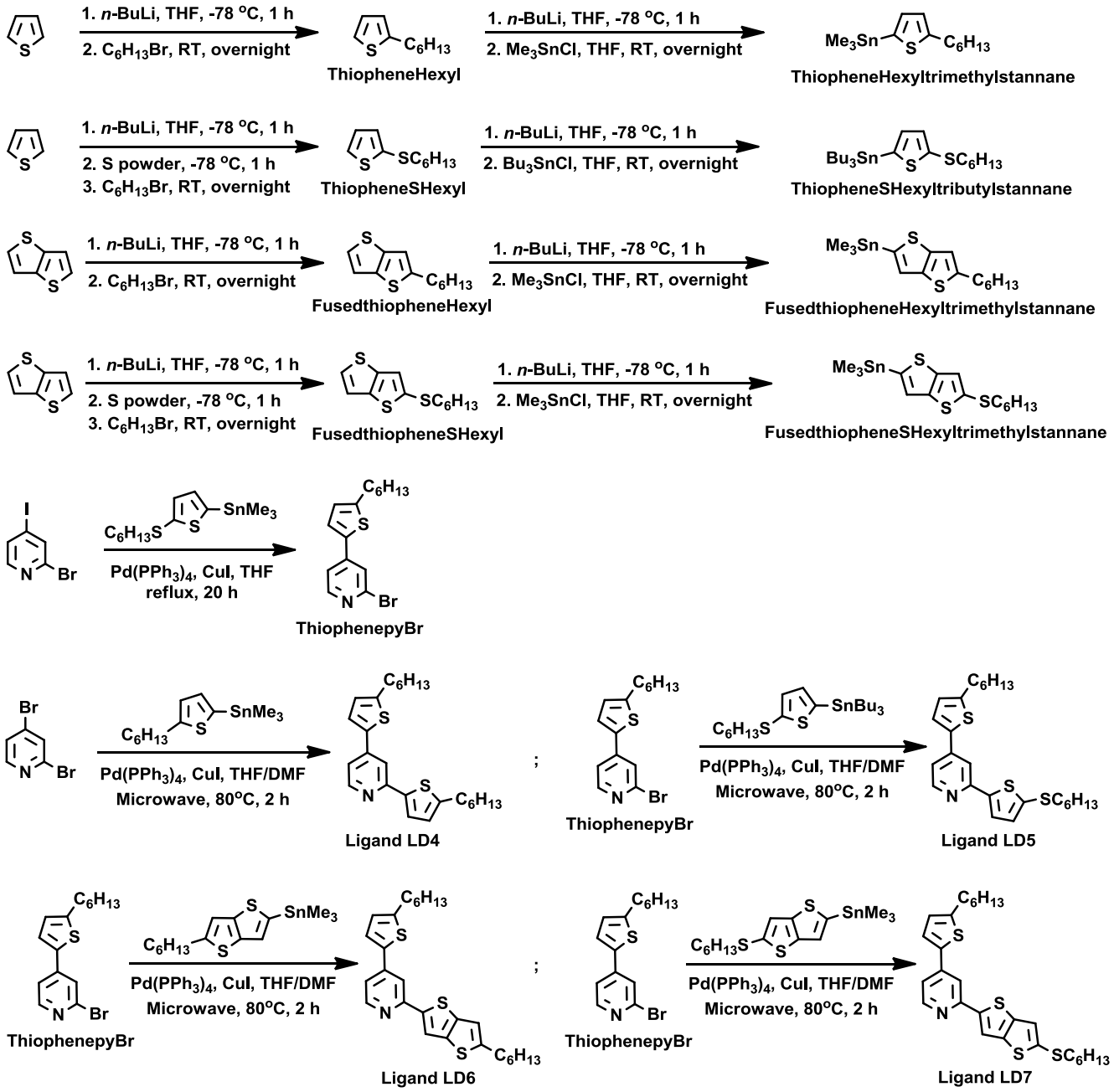
The-Duy Nguyen, Yan-Bo Lan, Chun-Guey Wu*

Department of Chemistry and Research Center for New Generation Photovoltaics, National Central University, Jhong-Li 32001, Taiwan, ROC

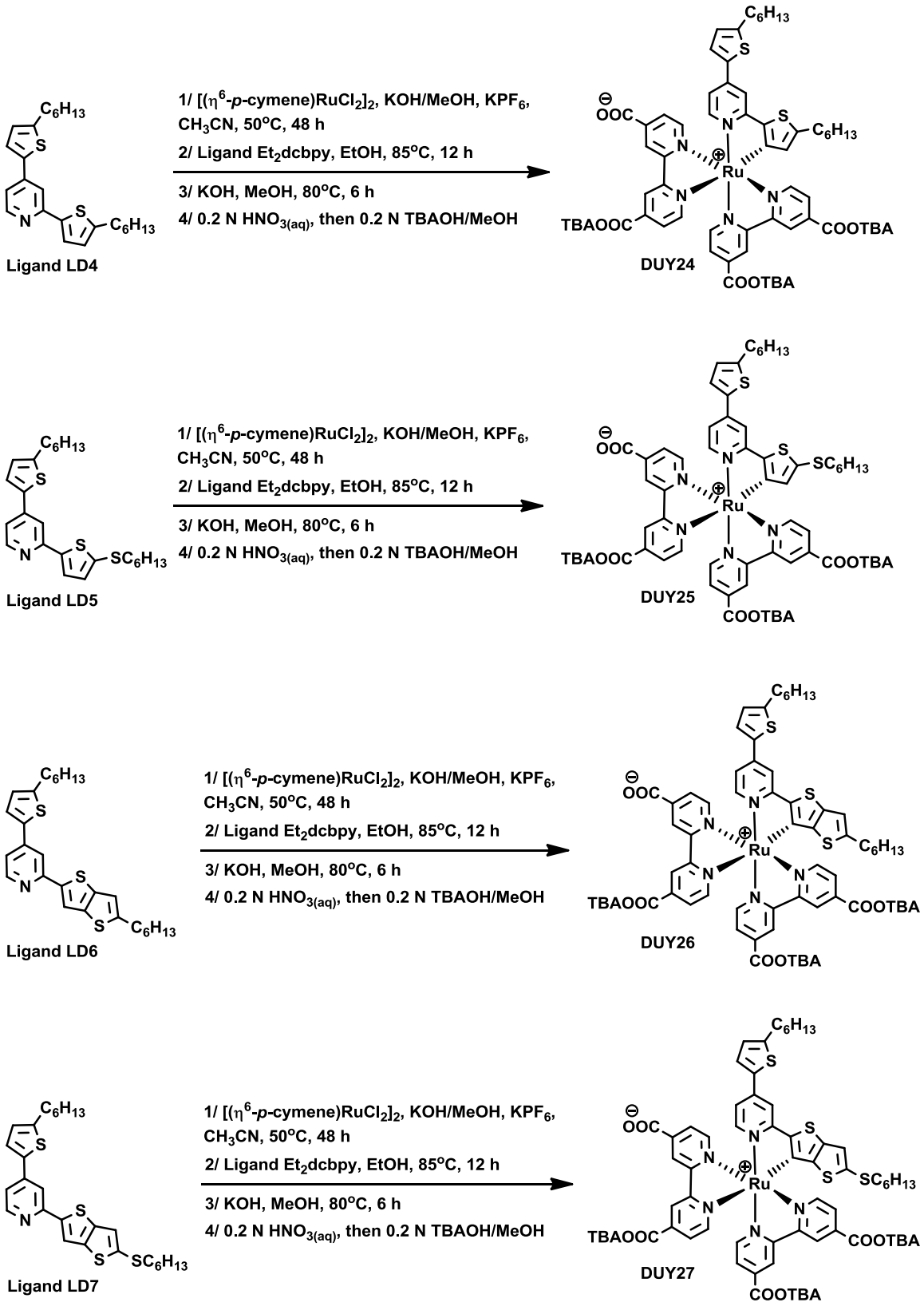
E-mail address of Professor C. G. Wu: t610002@cc.ncu.edu.tw

A. Synthesis

The preparation of the ligands (LD4-LD7) and complexes (DUY24~DUY27) is outlined in Scheme 1 and Scheme 2, respectively. The detailed synthetic procedures are described as the following:



Scheme 1. Syntheses of ligands LD4-LD7



Scheme 2. Syntheses of DUY24-DUY27

1. Preparation of ThiopheneHexyl

Thiophene (10 g, 119 mmol) was dissolved in 100 mL anhydrous THF, and then was cooled to -78^{o}C. 48 mL (120 mmol) of *n*-BuLi (2.5 M in hexane) was added dropwise to the solution which under continuously stirring for 1 h at -78^{o}C. 1-Bromohexane (19.62 g, 119 mmol) was added dropwise to the mixture and then stirred continuously overnight at room temperature. The reaction was terminated by adding deionized water and then extracted the product with CH_2Cl_2. The organic layer was collected and further purified by column chromatography using hexane as an eluent to afford 17.78 g of ThiopheneHexyl as yellowish oil. Yield: 89%. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.10 (1H, *dd*, J_1 = 5.1 Hz, J_2 = 1.2 Hz), 6.91 (1H, *dd*, J_1 = 5.1 Hz, J_2 = 3.3 Hz), 6.78 (1H, *dd*, J_1 = 3.3 Hz, J_2 = 1.2 Hz), 2.82 (2H, *t*, J = 7.5 Hz), 1.67 (2H, *m*), 1.31 (6H, *m*), 0.89 (3H, *t*, J = 7.2 Hz).

2. Preparation of ThiopheneSHexyl

Thiophene (2.5 g, 29.8 mmol) was dissolved in 30 mL anhydrous THF, and then was cooled to -78^{o}C. 12 mL (30 mmol) of *n*-BuLi (2.5 M in hexane) was added dropwise to the solution which under continuously stirring for 1 h at -78^{o}C. Sulfur powder (0.953 g, 29.8 mmol) was added to the reaction mixture and stirred continuously at -78^{o}C for another 1 h. 1-Bromohexane (4.905 g, 29.8 mmol) was added dropwise to the mixture and then stirred continuously overnight at room temperature. The reaction was terminated by adding water and then extracted the product with CH_2Cl_2. The organic layer was dried and further purified by column chromatography using hexane as an eluent to afford 5.75 g of ThiopheneSHexyl as yellowish oil. Yield: 97%. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.32 (1H, *dd*, J_1 = 5.4 Hz, J_2 = 1.2 Hz), 7.10 (1H, *dd*, J_1 = 3.6 Hz, J_2 = 1.2 Hz), 6.97 (1H, *dd*, J_1 = 5.4 Hz, J_2 = 3.6 Hz), 2.79 (2H, *t*, J = 7.2 Hz), 1.39 (2H, *m*), 1.27 (6H, *m*), 0.88 (3H, *t*, J = 6.3 Hz).

3. Preparation of FusedthiopheneHexyl

Thieno[3,2-b]thiophene (2.71 g, 19 mmol) was dissolved in 35 mL anhydrous THF, and then cooled to -78^{o}C. 8 mL (20 mmol) of *n*-BuLi (2.5 M in hexane) was added dropwise to the solution which under continuously stirring for 1 h at -78^{o}C. 1-Bromohexane (3.19 g, 19 mmol) was added dropwise to the mixture and then stirred continuously overnight at room temperature. The reaction was terminated by adding deionized water then extracted the product with CH_2Cl_2. The organic layer was collected and further purified by C18 reversed-phase column chromatography using methanol as an eluent to afford 2.42 g of FusedthiopheneHexyl as yellowish oil. Yield: 56%. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.26 (1H, *d*, J = 5.1 Hz), 7.18 (1H, *d*, J = 5.1 Hz), 6.95 (1H, *s*), 2.87 (2H, *t*, J = 7.5 Hz), 1.71 (2H, *pentet*, J = 7.2 Hz), 1.33 (6H, *m*), 0.89 (3H, *t*, J = 6.9 Hz).

4. Preparation of FusedthiopheneSHexyl

Thieno[3,2-b]thiophene (2.51 g, 18 mmol) was dissolved in 25 mL anhydrous THF, and then was cooled to -78^{o}C. 7.2 mL (18 mmol) of *n*-BuLi (2.5 M in hexane) was added dropwise to the solution which under continuously stirring for 1 h at -78^{o}C. 0.57 g (18 mmol) of sulfur powder was added to the reaction mixture and stirred continuously at -78^{o}C for another 1 h. 1-Bromohexane (2.96 g, 18 mmol) was added dropwise to the mixture and then stirred continuously overnight at room temperature. The reaction was terminated by adding water then extracted the product with CH_2Cl_2. The organic layer was dried and further purified by column chromatography using hexane as an eluent to afford 3.88 g of FusedthiopheneSHexyl as yellowish oil. Yield: 85%. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.40 (1H, *d*, J = 5.1 Hz), 7.32 (1H, *s*), 7.19 (1H, *d*, J = 5.1 Hz), 2.84 (2H, *t*, J = 7.2 Hz), 1.64 (2H, *pentet*, J = 6.6 Hz), 1.29 (6H, *m*), 0.88 (3H, *t*, J = 6.3 Hz).

5. Preparation of ThiopheneHexyltrimethylstannane

ThiopheneHexyl (8.89 g, 53 mmol) was dissolved in 50 mL dried THF and then cooled to -78^{o}C. 22.5 mL (56.5 mmol) of *n*-BuLi (2.5 M in hexane) was added dropwise to the solution and stirred for 1 h at -78^{o}C. A quantity of trimethyltin chloride (10.5 g, 53 mmol) dissolved in THF was added to the reaction mixture and stirred continuously overnight at room temperature. The reaction was terminated by adding deionized water and then extracted the product with CH_2Cl_2. The organic layer was dried to afford 16.87 g of ThiopheneHexyltrimethylstannane. Yield: 96%. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.01 (1H, *d*, J = 3.3 Hz), 6.90 (1H, *m*), 2.85 (2H, *t*, J = 7.5 Hz), 1.68 (2H, *pentet*, d = 7.8 Hz), 1.31 (6H, *m*), 0.89 (3H, *t*, J = 6.3 Hz), 0.34 (9H, *s*).

6. Preparation of ThiopheneSHexyltributylstannane

ThiopheneSHexyl (3 g, 15 mmol) was dissolved in 25 mL anhydrous THF and then cooled to -78^{o}C. 6.3 mL (15.5 mmol) of *n*-BuLi (2.5 M in hexane) was added dropwise to the solution and stirred for 1 h at -78^{o}C. A quantity of tributyltin chloride (4.9 g, 15 mmol) dissolved in THF was added to the reaction mixture and stirred continuously overnight at room temperature. The reaction was terminated by adding deionized water and then extracted the product with CH_2Cl_2. The organic layer was dried to afford 7.7 g of ThiopheneSHexyltributylstannane. Yield: 100%. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.17 (1H, *d*, J = 3.3 Hz), 7.03 (1H, *d*, J = 3.3 Hz), 2.81 (2H, *t*, J = 7.2 Hz), 1.57 (8H, *m*), 1.32 (18H, *m*), 0.89 (12H, *m*).

7. Preparation of FusedthiopheneHexyltrimethylstannane

FusedthiopheneHexyl (2.42 g, 11 mmol) was dissolved in 40 mL anhydrous THF and then cooled to -78^{o}C. 4.5 mL (11 mmol) of *n*-BuLi (2.5 M in hexane) was added dropwise to the solution and

stirred for 1 h at -78^{o}C. A quantity of trimethyltin chloride (2.15 g, 11 mmol) dissolved in THF was added to the reaction mixture and stirred continuously overnight at room temperature. The reaction was terminated by adding deionized water and then extracted the product with CH_2Cl_2. The organic layer was dried to afford 4.2 g of FusedthiopheneHexyltrimethylstannane. Yield: almost 100%. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.21 (1H, *s*), 6.95 (1H, *s*), 2.86 (2H, *t*, J = 7.2 Hz), 1.70 (2H, *pentet*, J = 7.2 Hz), 1.31 (6H, *m*), 0.89 (3H, *t*, J = 6.9 Hz), 0.39 (9H, *s*).

8. Preparation of FusedthiopheneSHexyltrimethylstannane

FusedthiopheneSHexyl (3.77 g, 15 mmol) was dissolved in 40 mL anhydrous THF and then cooled to -78^{o}C. 6 mL (15 mmol) of *n*-BuLi (2.5 M in hexane) was added dropwise to the solution and stirred for 1 h at -78^{o}C. A quantity of trimethyltin chloride (2.93 g, 15 mmol) dissolved in THF was added to the reaction mixture and stirred continuously overnight at room temperature. The reaction was terminated by adding deionized water and then extracted the product with CH_2Cl_2. The organic layer was dried to afford 6.05 g of FusedthiopheneSHexyltrimethylstannane. Yield: 98%. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.31 (1H, *s*), 7.22 (1H, *s*), 2.82 (2H, *t*, J = 7.2 Hz), 1.63 (2H, *m*), 1.23 (6H, *m*), 0.88 (3H, *t*, J = 6.3 Hz), 0.40 (9H, *s*).

9. Preparation of ThiophenepyBr

ThiopheneHexyltrimethylstannane (12 g, 36 mmol), 2-bromo-4-iodopyridine (10 g, 35 mmol), $Pd(PPh_3)_4$ (2 g, 1.73 mmol), and CuI (0.67 g, 3.52 mmol) were mixed in anhydrous THF (100 mL) and refluxed for 20 h. The resulting solution was dried under reduced pressure, then extracted the product with CH_2Cl_2. The organic layer was collected and further purified by C18 reversed-phase column chromatography using methanol as an eluent to afford 5.7 g of ThiophenepyBr as yellowish solid. Yield: 50%. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.26 (1H, *d*, J = 5.1 Hz), 7.58 (1H, *m*), 7.33 (1H, *dd*, J_1 = 5.4 Hz, J_2 = 1.8 Hz), 7.31 (1H, *d*, J = 3.6 Hz), 6.79 (1H, *d*, J = 3.6 Hz), 2.82 (2H, *t*, J = 7.8 Hz), 1.69 (2H, *pentet*, J = 7.5 Hz), 1.35 (6H, *m*), 0.89 (3H, *t*, J = 6.9 Hz).

10. Preparation of ligand LD4

ThiopheneHexyltrimethylstannane (4.2 g, 13 mmol), 2,4-dibromopyridine (1.5 g, 6.3 mmol), $Pd(PPh_3)_4$ (0.36 g, 0.33 mmol), and CuI (0.12 g, 0.63 mmol) were mixed in a THF-DMF mixed solvent (30 ml THF + 10 ml DMF) and refluxed for 2 h under microwave condition (temperature 80^{o}C, frequency 400 MHz). The resulting solution was dried under reduced pressure and then extracted the product with CH_2Cl_2. The organic layer was dried and further purified by C18 reversed-phase column chromatography using methanol as an eluent to afford 1.45 g of LD4 as yellowish solid. Yield: 56%. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.46 (1H, *dd*, J_1 = 5.1 Hz, J_2 = 0.6 Hz), 7.70 (1H, *dd*, J_1 = 1.5 Hz, J_2 =

0.6 Hz), 7.45 (1H, *d*, J = 3.6 Hz), 7.35 (1H, *d*, J = 3.6 Hz), 7.23 (1H, *dd*, J_1 = 5.1 Hz, J_2 = 1.8 Hz), 6.81 (1H, *d*, J = 3.3 Hz), 6.80 (1H, *d*, J = 3.6 Hz), 2.84 (4H, *t*, J = 7.5 Hz), 1.72 (4H, *pentet*, J = 6.9 Hz), 1.34 (12H, *m*), 0.90 (6H, *m*).

11. Preparation of ligand LD5

ThiopheneSHexyltributylstannane (3.5 g, 6.8 mmol), ThiophenepyBr (2 g, 6.2 mmol), $Pd(PPh_3)_4$ (0.35 g, 0.3 mmol), and CuI (0.12 g, 0.6 mmol) were mixed in a THF-DMF mixed solvent (100 ml THF + 30 ml DMF) and refluxed for 2 h under microwave condition (temperature 80^{o}C, frequency 400 MHz). The resulting solution was dried under reduced pressure, then extracted the product with CH_2Cl_2. The organic layer was collected and further purified by C18 reversed-phase column chromatography using methanol as an eluent to afford 1.1 g of LD5 as yellowish solid. Yield: 39%. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 8.48 (1H, *dd*, J_1 = 3.0 Hz, J_2 = 0.3 Hz), 7.69 (1H, *d*, J = 0.6 Hz), 7.47 (1H, *d*, J = 2.4 Hz), 7.36 (1H, *d*, J = 2.1 Hz), 7.27 (1H, *dd*, J_1 = 3.3 Hz, J_2 = 1.2 Hz), 7.08 (1H, *d*, J = 2.1 Hz), 6.82 (1H, *d*, J = 2.1 Hz), 2.87 (4H, *m*), 1.69 (4H, *m*), 1.35 (12H, *m*), 0.89 (6H, *m*).

12. Preparation of ligand LD6

FusedthiopheneHexyltrimethylstannane (3 g, 7.2 mmol), ThiophenepyBr (1.5 g, 4.6 mmol), $Pd(PPh_3)_4$ (0.27 g, 0.23 mmol), and CuI (0.09 g, 0.47 mmol) were mixed in a THF-DMF mixed solvent (100 ml THF + 30 ml DMF) and refluxed for 2 h under microwave condition (temperature 80^{o}C, frequency 400 MHz). The resulting solution was dried under reduced pressure, then extracted the product with CH_2Cl_2. The organic layer was dried and further purified by C18 reversed-phase column chromatography using methanol as an eluent to afford 1.4 g of LD6 as yellowish solid. Yield: 60%. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.49 (1H, *d*, J = 5.4 Hz), 7.75 (2H, *s*), 7.37 (1H, *d*, J = 3.0 Hz), 7.27 (1H, *d*, J = 1.5 Hz), 6.98 (1H, *s*), 6.82 (1H, *dd*, J_1 = 3.6 Hz, J_2 = 0.6 Hz), 2.87 (4H, *m*), 1.73 (4H, *m*), 1.37 (12H, *m*), 0.90 (6H, *m*).

13. Preparation of ligand LD7

FusedthiopheneSHexyltrimethylstannane (2.5 g, 6.5 mmol), ThiophenepyBr (1.5 g, 4.6 mmol), $Pd(PPh_3)_4$ (0.27 g, 0.23 mmol), and CuI (0.09 g, 0.47 mmol) were mixed in a THF-DMF mixed solvent (100 ml THF + 30 ml DMF) and refluxed for 2 h under microwave condition (temperature 80^{o}C, frequency 400 MHz). The resulting solution was dried under reduced pressure, then extracted the product with CH_2Cl_2. The organic layer was dried and further purified by C18 reversed-phase column chromatography using methanol as an eluent to afford 1.6 g of LD7 as yellowish solid. Yield: 54%. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.50 (1H, *d*, J = 5.1 Hz), 7.76 (1H, *s*), 7.74 (1H, *s*), 7.37 (1H, *d*, J = 3.6 Hz),

7.31 (1H, *s*), 7.29 (1H, *dd*, J_1 = 5.4 Hz, J_2 = 4.2 Hz), 6.82 (1H, *d*, J = 3.0 Hz), 2.86 (4H, *m*), 1.69 (4H, *m*), 1.32 (12H, *m*), 0.89 (6H, *m*).

14. Preparation of DUY24

A 0.5 ml methanol solution of KOH (0.035 g, 0.6 mmol) was added to a mixture of LD4 (0.25 g, 0.6 mmol), $[(\eta^6\text{-}p\text{-cymene})RuCl_2]_2$ (0.185 g, 0.3 mmol), and KPF_6 (0.223 g, 1.2 mmol) in acetonitrile (8 mL). The mixture was stirred at 50°C for 2 days. The solvent was then removed in vacuo, then purified by column chromatography [SiO_2, CH_2Cl_2/MeOH = 9/1]. The yellow-orange main band was collected and dried. A 50 mL ethanol solution containing the yellow-orange band and Et_2dcbpy (1.363 g, 1.2 mmol) was stirred overnight at 85°C. The solution was dried in vacuo, then purified by column chromatography using CH_2Cl_2/MeOH = 9/1 as an eluent. The dark main band was collected and dried. A 100 mL methanol solution containing the dark band and KOH (0.15 g, 2.7 mmol) was stirred for 6 h at 80°C. The solvent was then removed in vacuo. The crude product was reconstituted in a minimum volume of MeOH and then purified by Sephadex LH-20 column chromatography (MeOH as an eluent). The dark-red band was collected and the solvent was reduced to about 10 ml, then an excess amount of 0.2 N $HNO_{3(aq)}$ was added dropwise to precipitate the acidic form of DUY24. The precipitate was filtered and then dissolved in a 0.2 M TBAOH methanol solution. Methanol was removed, and the resulting solid was purified by C18 reversed-phase gel chromatography (using MeOH/H_2O = 7/3 as an eluent) to obtain DUY24 as dark-red sticky solid (0.75 g, yield 63%). ^{1}H-NMR (500 MHz, CD_3OD): δ 9.03 (1H, *s*), 8.97 (1H, *s*), 8.90 (2H, *s*), 8.17 (1H, *d*, J = 6.0 Hz), 8.09 (1H, *d*, J = 6.0 Hz), 7.89 (1H, *dd*, J_1 = 5.5 Hz, J_2 = 1.5 Hz), 7.87 (1H, *s*), 7.86 (1H, *s*), 7.77 (1H, *dd*, J_1 = 6.0 Hz, J_2 = 1.5 Hz), 7.72 (1H, *dd*, J_1 = 5.5 Hz, J_2 = 1.0 Hz), 7.69 (1H, *dd*, J_1 = 6.2 Hz, J_2 = 1.0 Hz), 7.47 (1H, *d*, J = 1.5 Hz), 7.31 (1H, *d*, J = 4.0 Hz), 7.28 (1H, *d*, J = 6.0 Hz), 6.88 (1H, *dd*, J_1 = 6.0 Hz, J_2 = 2.0 Hz), 6.74 (1H, *d*, J = 3.5 Hz), 6.05 (1H, *s*), 3.21 (24H, *t*, J = 8.0 Hz), 2.74 (4H, *t*, J = 7.5 Hz), 1.62 (28H, *m*), 1.36 (24H, *sextet*, J = 7.5 Hz), 1.31-1.24 (12H, *m*), 0.94 (36H, *t*, J = 7.5 Hz), 0.84 (6H, *t*, J = 6.5 Hz). HRMS (ESI): calcd for $[M+H]^+$: 1724.0296; Found: 1724.0283. Elemental analysis: calcd for $C_{97}H_{152}N_8O_8RuS_2.11H_2O.0.25$TBA: C, 61.20; H, 9.31; N, 5.83; S, 3.24; Found: C, 61.32; H, 9.36; N, 5.82; S, 3.12.

15. Preparation of DUY25

A 0.5 ml methanol solution of KOH (0.035 g, 0.63 mmol) was added to a mixture of LD5 (0.268 g, 0.6 mmol), $[(\eta^6\text{-}p\text{-cymene})RuCl_2]_2$ (0.185 g, 0.3 mmol), and KPF_6 (0.223 g, 1.2 mmol) in acetonitrile (8 ml). The mixture was stirred at 50°C for 2 days. The solvent was then removed in vacuo, then purified by column chromatography [SiO_2, CH_2Cl_2/MeOH = 9/1]. The yellow-orange main band was collected and dried. A 50 mL ethanol solution containing the yellow-orange band and Et_2dcbpy (0.363

g, 1.2 mmol) were stirred overnight at 85^{o}C. The solution was dried in vacuo, then purified by column chromatography using CH_2Cl_2/MeOH = 9/1 as an eluent. The dark main band was collected and dried. A 25 mL methanol solution containing the dark band and KOH (0.15 g, 2.7 mmol) was stirred for 6 h at 80^{o}C. The solvent was then removed in vacuo. The crude product was reconstituted in a minimum volume of MeOH and then purified by Sephadex LH-20 column chromatography (MeOH as an eluent). The dark-red band was collected and the solvent was reduced to about 10 ml, then an excess amount of 0.2 N $HNO_{3(aq)}$ was added dropwise to precipitate the acidic form of DUY25. The precipitate was filtered and then dissolved in a 0.2 M TBAOH methanol solution. Methanol was removed, and the resulting solid was purified by C18 reversed-phase gel chromatography (using MeOH/H_2O = 7/3 as an eluent) to obtain DUY25 as dark-red sticky solid (0.85 g, yield 71%). ^{1}H-NMR (500 MHz, CD_3OD): δ 9.02 (1H, *s*), 8.94 (1H, *d*, J = 1.0 Hz), 8.89 (1H, *d*, J = 1.5 Hz), 8.88 (1H, *d*, J = 1.0 Hz), 8.14 (1H, *d*, J = 6.0 Hz), 8.02 (1H, *d*, J = 6.0 Hz), 7.90 (1H, *d*, J = 5.5 Hz), 7.88 (1H, *d*, J = 6.0 Hz), 7.86 (1H, *dd*, J_1 = 5.5 Hz, J_2 = 1.5 Hz), 7.74 (1H, *dd*, J_1 = 6.0 Hz, J_2 = 2.0 Hz), 7.69 (1H, *dd*, J_1 = 2.5 Hz, J_2 = 1.5 Hz), 7.68 (1H, *dd*, J_1 = 3.0 Hz, J_2 = 2.0 Hz), 7.56 (1H, *d*, J = 1.5 Hz), 7.47 (1H, *d*, J = 3.5 Hz), 7.26 (1H, *d*, J = 6.0 Hz), 6.97 (1H, *dd*, J_1 = 6.0 Hz, J_2 = 2.0 Hz), 6.84 (1H, *d*, J = 3.5 Hz), 6.17 (1H, *s*), 3.22 (24H, *m*), 2.85 (2H, *t*, J = 7.5 Hz), 2.78 (2H, *dt*, J_1 = 7.0 Hz, J_2 = 2.0 Hz), 1.70 (2H, *pentet*, J = 7.5 Hz), 1.64 (24H, *m*), 1.54 (2H, *pentet*, J = 7.0 Hz), 1.39 (24H, *sextet*, J = 7.5 Hz), 1.34-1.23 (12H, *m*), 1.00 (36H, *t*, J = 7.0 Hz), 0.90 (3H, *t*, J = 7.0 Hz), 0.88 (3H, *t*, J = 7.0 Hz). HRMS (ESI): calcd for $[M+H]^+$: 1756.0017; Found: 1755.9940. Elemental analysis: calcd for $C_{97}H_{152}N_8O_8RuS_3.10H_2O.0.25TBA$: C, 60.77; H, 9.14; N, 5.79; S, 4.82; Found: C, 61.04; H, 9.21; N, 5.94; S, 5.01.

16. Preparation of DUY26

A 1 ml methanol solution of KOH (0.065 g, 1.2 mmol) was added to a mixture of LD6 (0.525 g, 1.1 mmol), $[(\eta^6$-*p*-cymene)$RuCl_2]_2$ (0.35 g, 0.6 mmol), and KPF_6 (0.84 g, 2.2 mmol) in acetonitrile (12 ml). The mixture was stirred at 50^{o}C for 2 days. The solvent was then removed in vacuo, then purified by column chromatography [SiO_2, CH_2Cl_2/MeOH = 9/1]. The yellow-orange main band was collected and dried. A 50 ml ethanol solution containing the yellow-orange band and Et_2dcbpy (0.676 g, 2.3 mmol) was stirred overnight at 85^{o}C. The solution was dried in vacuo, then purified by column chromatography using CH_2Cl_2/MeOH = 9/1 as an eluent. The dark main band was collected and dried. A 25 ml methanol solution containing the dark band and KOH (0.28 g, 5 mmol) was stirred for 6 h at 80^{o}C. The solvent was then removed in vacuo. The crude product was reconstituted in a minimum volume of MeOH and then purified by Sephadex LH-20 column chromatography (MeOH as an eluent). The dark-red band was collected and the solvent was reduced to about 10 ml, then an excess amount of 0.2 N $HNO_{3(aq)}$ was added dropwise to precipitate the acidic form of DUY26. The precipitate was

filtered and then dissolved in a 0.2 M TBAOH methanol solution. Methanol was removed, and the resulting solid was purified by C18 reversed-phase silica gel chromatography (using MeOH/H_2O = 7/3 as an eluent) to obtain DUY26 as dark-red sticky solid (1.34 g, yield 59%). ^{1}H-NMR (500 MHz, CD_3OD): δ 9.03 (1H, *s*), 8.94 (1H, *d*, J = 1.5 Hz), 8.93 (1H, *d*, J = 1.0 Hz), 8.86 (1H, *d*, J = 1.0 Hz), 8.09 (1H, *d*, J = 6.0 Hz), 8.00 (1H, *d*, J = 5.5 Hz), 7.95 (1H, *d*, J = 6.0 Hz), 7.87 (1H, *dd*, J_1 = 5.5 Hz, J_2 = 1.5 Hz), 7.85 (1H, *dd*, J_1 = 5.5 Hz, J_2 = 1.5 Hz), 7.75 (1H, *dd*, J_1 = 6.0 Hz, J_2 = 1.5 Hz), 7.72 (1H, *dd*, J_1 = 6.0 Hz, J_2 = 2.0 Hz), 7.64 (1H, *dd*, J_1 = 5.5 Hz, J_2 = 1.5 Hz), 7.55 (1H, *d*, J = 1.5 Hz), 7.46 (1H, *d*, J = 3.5 Hz), 7.24 (1H, *d*, J = 6.5 Hz), 6.93 (1H, *s*), 6.92 (1H, *dd*, J_1 = 6.0 Hz, J_2 = 2.0 Hz), 6.85 (1H, *d*, J = 4.0 Hz), 3.21 (24H, *m*), 2.86 (2H, *t*, J = 7.5 Hz), 2.67 (2H, *t*, J = 7.0 Hz), 1.70 (2H, *pentet*, J = 7.5 Hz), 1.63 (24H, *m*), 1.53 (2H, *pentet*, J = 8.0 Hz), 1.38 (24H, *sextet*, J = 7.5 Hz), 1.34-1.28 (12H, *m*), 0.99 (36H, *t*, J = 7.5 Hz), 0.91 (3H, *t*, J = 7.0 Hz), 0.88 (3H, *t*, J = 7.0 Hz). HRMS (ESI): calcd for $[M+H]^+$: 1780.0017; Found: 1779.9987. Elemental analysis: calcd for $C_{99}H_{152}N_8O_8RuS_3.10H_2O.0.25TBA$: C, 61.23; H, 9.03; N, 5.72; S, 4.76; Found: C, 61.46; H, 9.03; N, 5.77; S, 4.94.

17. Preparation of DUY27

A 1.0 mL methanol solution of KOH (0.065 g, 1.2 mmol) was added to a mixture of LD7 (0.575 g, 1.2 mmol), $[(\eta^6$-*p*-cymene)$RuCl_2]_2$ (0.35 g, 0.6 mmol), and KPF_6 (0.42 g, 2.2 mmol) in acetonitrile (12 ml). The mixture was stirred at 50^{o}C for 2 days. The solvent was then removed in vacuo, then purified by column chromatography [SiO_2, CH_2Cl_2/MeOH = 9/1]. The yellow-orange main band was collected and dried. A 50 ml ethanol solution containing the yellow-orange band and Et_2dcbpy (0.675 g, 2.3 mmol) was stirred overnight at 85^{o}C. The solution was dried in vacuo, then purified by column chromatography using CH_2Cl_2/MeOH = 9/1 as an eluent. The dark main band was collected and dried. A 25 mL methanol solution containing the dark band and KOH (0.28 g, 5 mmol) was stirred for 6 h at 80^{o}C. The solvent was then removed in vacuo. The crude product was reconstituted in a minimum volume of MeOH and then purified by Sephadex LH-20 column chromatography (MeOH is an eluent). The dark-red band was collected and the solvent was reduced to about 10 mL, then an excess amount of 0.2 N $HNO_{3(aq)}$ was added dropwise to precipitate the acidic form of DUY27. The precipitate was filtered and then dissolved in a 0.2 M TBAOH methanol solution. Methanol was removed, and the resulting solid was purified by C18 reversed-phase gel chromatography (using MeOH/H_2O = 7/3 as an eluent) to obtain DUY27 as dark-red sticky solid (1.6 g, yield 65%). ^{1}H-NMR (500 MHz, CD_3OD): δ 9.03 (1H, *s*), 8.954 (1H, *d*, J = 2.0 Hz), 8.950 (1H, *d*, J = 2.0 Hz), 8.87 (1H, *d*, J = 1.5 Hz), 8.07 (1H, *d*, J = 5.5 Hz), 7.98 (1H, *d*, J = 6.0 Hz), 7.97 (1H, *d*, J = 6.0 Hz), 7.87 (1H, *dd*, J_1 = 5.5 Hz, J_2 = 1.5 Hz), 7.85 (1H, *dd*, J_1 = 5.5 Hz, J_2 = 0.5 Hz), 7.78 (1H, *dd*, J_1 = 6.0 Hz, J_2 = 1.5 Hz), 7.72 (1H, *dd*, J_1 = 5.5

Hz, J_2 = 1.5 Hz), 7.65 (1H, *dd*, J_1 = 6.0 Hz, J_2 = 1.5 Hz), 7.62 (1H, *d*, J = 1.5 Hz), 7.48 (1H, *d*, J = 3.5 Hz), 7.27 (1H, *dd*, J_1 = 6.0 Hz, J_2 = 0.5 Hz), 7.25 (1H, *s*), 6.98 (1H, *dd*, J_1 = 6.0 Hz, J_2 = 2.0 Hz), 6.86 (1H, *d*, J = 4.0 Hz), 3.22 (24H, *m*), 2.86 (2H, *t*, J = 7.5 Hz), 2.69 (2H, *t*, J = 7.5 Hz), 1.71 (2H, *pentet*, J = 7.5 Hz), 1.64 (24H, *m*), 1.52 (2H, *pentet*, J = 7.5 Hz), 1.39 (24H, *sextet*, J = 7.5 Hz), 1.34-1.23 (12H, *m*), 0.99 (36H, *t*, J = 7.5 Hz), 0.91 (3H, *t*, J = 7.0 Hz), 0.87 (3H, *t*, J = 7.0 Hz). HRMS (ESI): calcd for $[M+H]^+$: 1811.9738; Found: 1811.9712. Elemental analysis: calcd for $C_{99}H_{152}N_8O_8RuS_4.9H_2O.0.25TBA$: C, 60.80; H, 8.87; N, 5.68; S, 6.30; Found: C, 60.89; H, 9.08; N, 5.72; S, 6.59.

B. Supplementary Tables and Figures

Table S1. Selective transition states with oscillator strength (*f*) larger than 0.01 for DUY24 in EtOH

State	Wavelength (λ, nm)	Oscillator Strength (*f*)	Transition assignment (only major orbital contributions; H = HOMO, L = LUMO)
1	786.54658	0.0146	H→L (74%), H→L+1 (10%)
4	605.68313	0.0748	H-2→L (37%), H-1→L (32%), H→L+2 (13%)
6	556.50315	0.186	H-2→L (15%), H→L+2 (57%)
7	515.71622	0.0896	H-2→L+1 (65%)
9	489.72365	0.0194	H-4→L (17%), H→L+3 (60%)
10	484.25316	0.0127	H-4→L (31%), H-2→L+2 (17%), H→L+4 (32%)
11	479.81167	0.0913	H-2→L+2 (17%), H→L+3 (21%), H→L+4 (48%)
12	466.82231	0.0289	H→L+5 (89%)
14	453.85217	0.1713	H-4→L (26%), H-4→L+1 (24%), H-2→L+2 (27%)
15	441.25324	0.208	H-4→L+1 (49%)
17	426.82228	0.0441	H-2→L+3 (24%), H-1→L+3 (67%)
18	421.19628	0.0347	H-2→L+3 (50%), H-2→L+4 (13%), H-1→L+3 (16%), H-1→L+4 (13%)
21	410.48648	0.217	H-2→L+4 (15%), H-2→L+5 (21%), H-1→L+4 (25%), H-1→L+5 (30%)
23	404.30228	0.0485	H-4→L+2 (55%), H-1→L+5 (24%)
25	402.76561	0.012	H-6→L (52%), H-2→L+5 (19%), H→L+6 (17%)
26	401.38346	0.0122	H-2→L+5 (10%), H→L+6 (72%)
28	387.61751	0.0239	H-5→L+1 (32%), H→L+7 (18%)
33	367.57586	0.155	H-8→L (43%), H→L+7 (37%)
34	359.79958	0.0549	H-8→L (24%), H-4→L+3 (13%), H-1→L+6 (41%)
37	355.39568	0.0205	H-4→L+3 (14%), H-2→L+6 (65%)
38	351.7158	0.2643	H-4→L+4 (59%), H→L+7 (15%)
39	347.20473	0.0101	H-4→L+5 (84%)
48	333.51267	0.0171	H-2→L+7 (16%), H-1→L+7 (75%)
49	328.78978	0.1866	H-2→L+7 (66%)
50	327.31418	0.0358	H-10→L (64%)
54	320.65209	0.0261	H-11→L+1 (60%), H-9→L (10%)
56	318.64951	0.1496	H-5→L+4 (50%), H-1→L+13 (15%)
57	317.8245	0.1434	H-12→L (11%), H-5→L+4 (32%), H-1→L+13 (20%), H→L+13 (11%)
60	312.44226	0.0598	H-12→L (23%), H-10→L+1 (26%), H-5→L+5 (22%)
61	311.65687	0.0224	H-10→L+1 (14%), H-5→L+5 (62%)
62	310.71182	0.275	H-12→L (19%), H-10→L+1 (26%), H-8→L+2 (17%), H→L+8 (18%)
63	308.24757	0.0907	H-12→L (18%), H→L+8 (65%)
65	307.40686	0.0382	H-7→L+4 (12%), H-4→L+6 (68%)

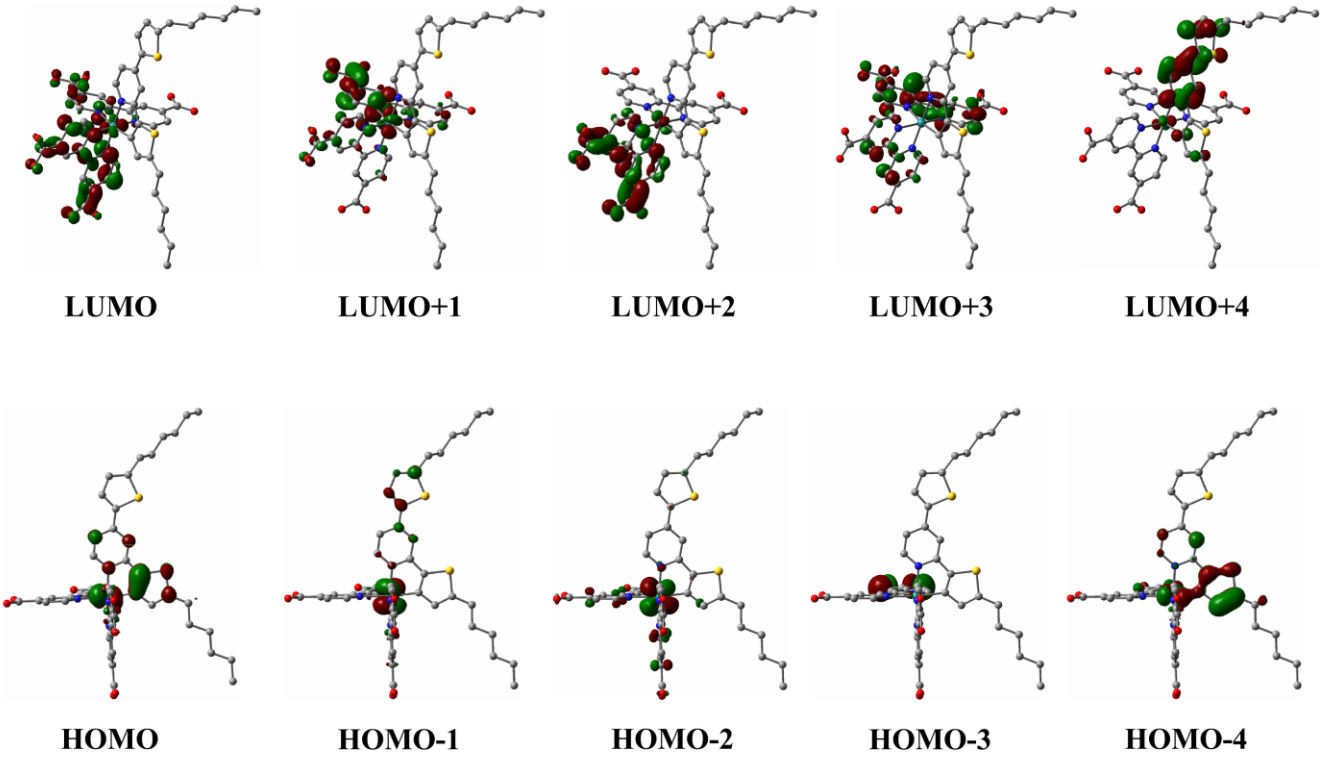


Figure S1. First ten frontier orbitals of DUY24 (isovalue = 0.04)

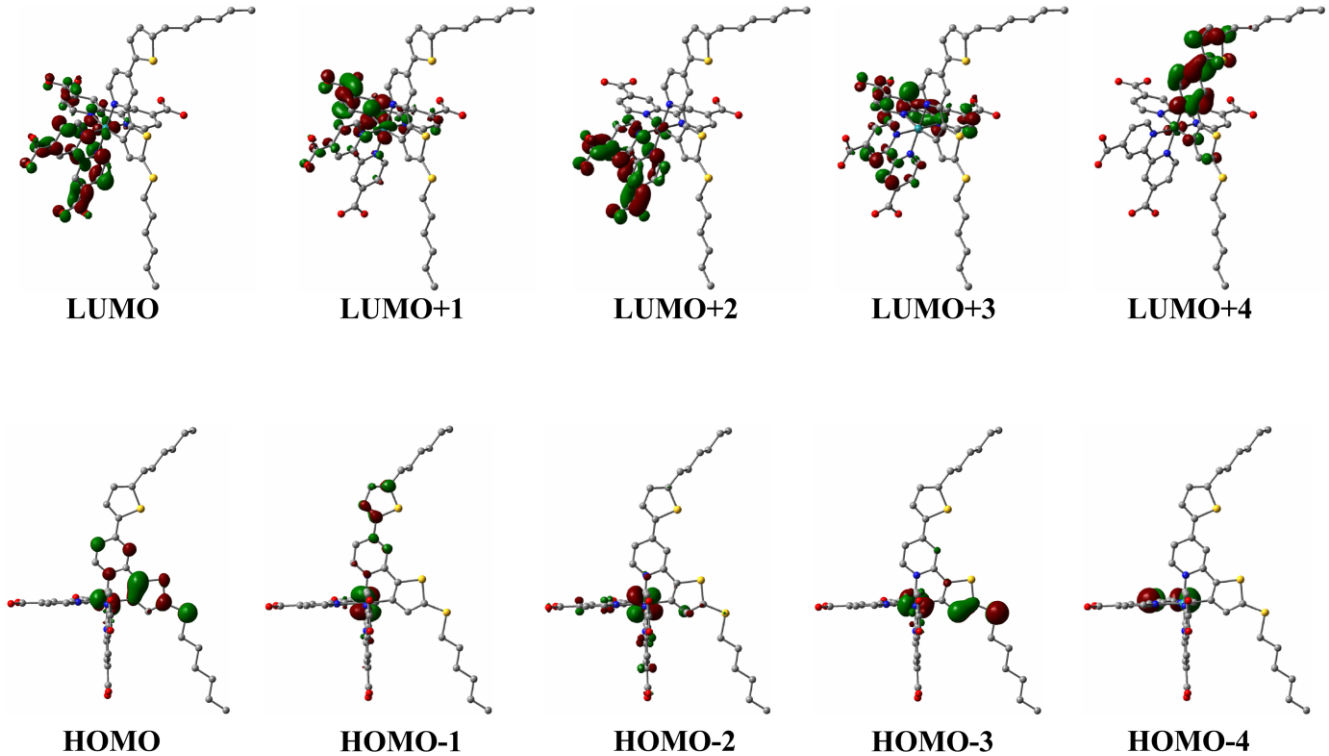


Figure S2. First ten frontier orbitals of DUY25 (isovalue = 0.04)

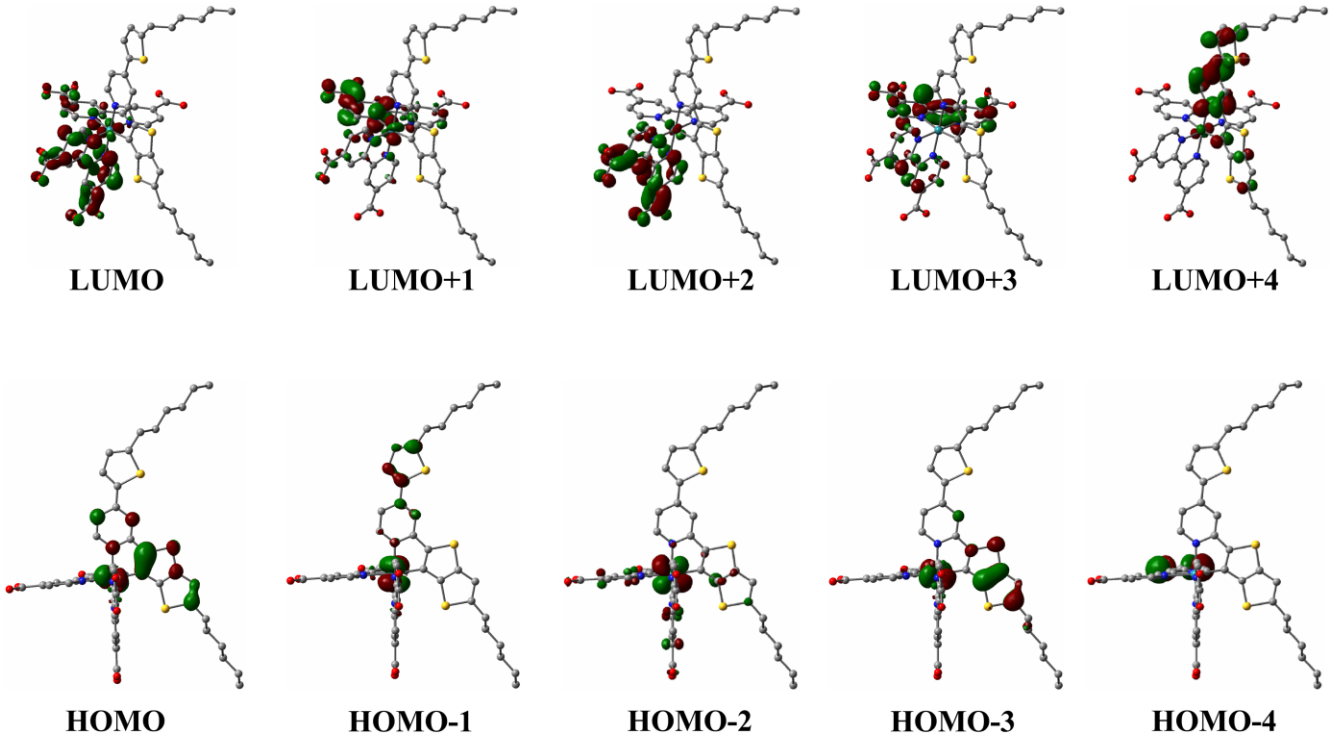


Figure S3. First ten frontier orbitals of DUY26 (isovalue = 0.04)

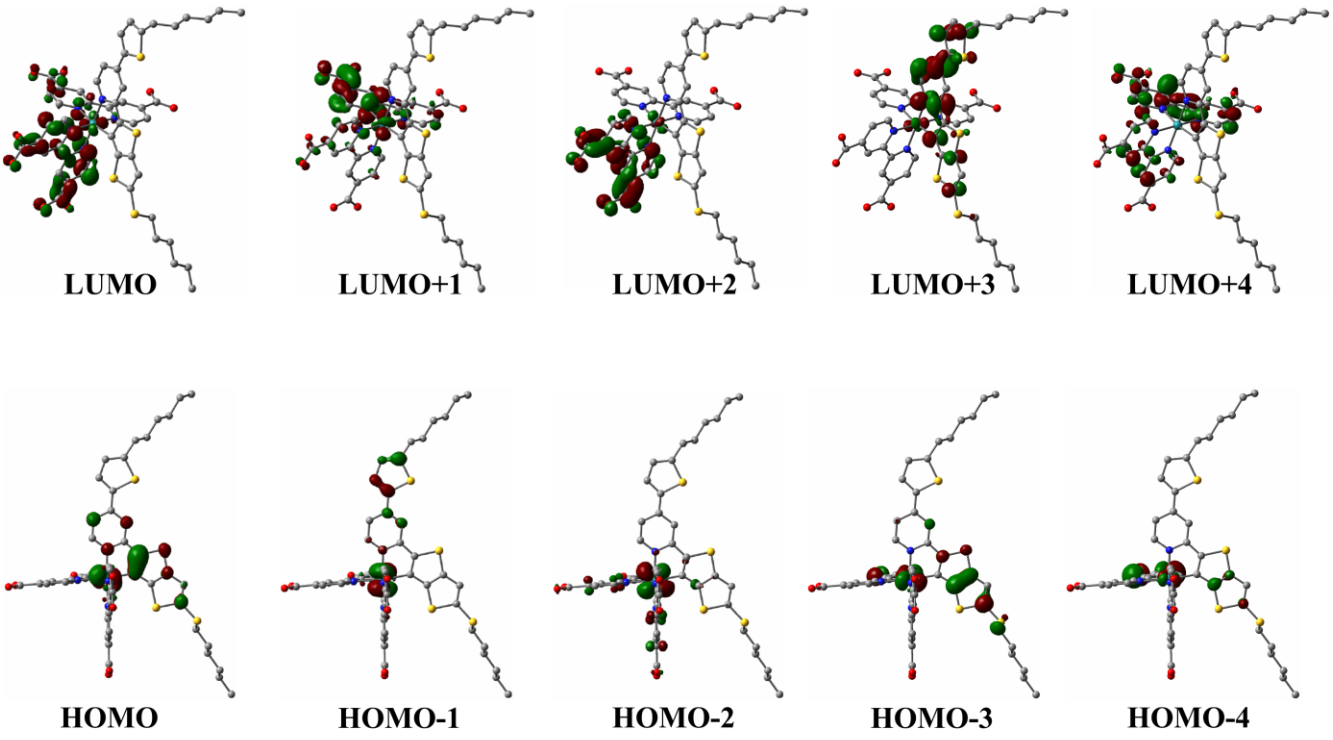


Figure S4. First ten frontier orbitals of DUY27 (isovalue = 0.04)