Electronic Supplementary Information

Photochromism and fluorescent properties of bisbenzothienylethene and S,S,S’,S’-tetraoxide derivatives with dual conjugated fluorescent groups on their side chains

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1. Experimental details

**Apparatus.** $^1$H-NMR spectra were recorded on a Bruker DRX300 (300 MHz). $^1$H-NMR chemical shifts in CDCl$_3$ were determined using tetramethylsilane (TMS) as an internal standard. MALDI-TOF-Mass spectra were recorded on a Shimadzu AXIMA-CFR. Electron impact mass spectra were measured with JEOL JMS-AX-600. Infrared absorption spectra were recorded with JASCO FT-IR-4100. Melting points were measured with Yazawa BY-2.

Chemical reactions were carried out under a dry N$_2$ atmosphere. All solvents including dry tetrahydrofuran (THF) were purchased and used as received. Flash column chromatography was carried out on 230-400 mesh silica gel using ethyl acetate and hexane as the eluent unless otherwise described. Analytical thin-layer chromatography was performed on the pre-coated 0.25 mm thick silica gel TLC plates.

A microwave heating apparatus (Boitage 11560) was used for the synthesis of 3o.

**Optical measurements.** Absorption spectra were recorded on a JASCO V-550. Fluorescence spectra were recorded on a JASCO FP-6500 spectrophotometer. Fluorescence quantum yields of 1 were determined using JASCO FP-6500 or FP-8500 spectrophotometers.

Photochemical reactions were carried out in a 10 mm length quartz cell. Photoirradiation with 313-nm light was carried out using a 500-W ultra-high-pressure mercury lamp (USHIO USH-500D or U1501HQ), separated by filters (a 5 cm water filter, a UV-31 glass filter, a UV-D33S glass filter, a 5 cm aqueous NiSO$_4$ filter, a 1 cm aqueous K$_2$CrO$_4$ filter and a 1 cm aqueous potassium hydrogenphthalate filter). Photoirradiation with 506-nm light was carried out using a 500-W Xenon lamp (USHIO UXL-500D-0), separated by filters (a 5 cm water filter, a Pyrex glass filter, a Y-47 glass filter and a KL-50 interference glass filter). Photoirradiation with 578-nm light was carried out using a 500-W Xenon lamp (USHIO UXL-500D-0), separated by filters (a 5 cm water filter, an O-54 glass filter and a KL-56 interference glass filter). Irradiation with >490-nm light was carried out using a 500-W Xenon lamp (USHIO UXL-500D-0), separated by filters (a 5 cm water filter, a Pyrex glass filter and a Y-49 glass filter). Irradiation with >540-nm light was carried out using a 500-W Xenon lamp (USHIO UXL-500D-0), separated by filters (a 5 cm water filter, a Pyrex glass filter and an O-54 glass filter).

**Computational details.** DFT geometry optimization and TD DFT calculations for absorption spectra were carried out with Spartan’16 (Wavefunction Inc.) at B3LYP/6-31G* level.

Synthesis of 10, 20, 30, 40 and 6 were carried out according to the following scheme.

Synthesis of 1,4-bis(dodecyloxy)-2-iodo-5-trimethylsilylhexynylbenzene (10)

To a solution of 9 [1] (1.01 g, 1.44 mmol), Pd(PPh3)2Cl2 (19.4 mg, 0.028 mmol, 0.019 eq), CuI (13.9 mg, 0.073 mmol, 0.051 eq) and triethylamine (25 ml) in a two-necked flask was added dropwise trimethylsilylacetylene (152 µL, 1.08 mmol, 0.75 eq), and the resulting solution was stirred at room temperature for overnight. The solvent was removed in vacuo, and 3 mol dm\(^{-3}\) aq. hydrochloric acid and CHCl\(_3\) were added. The organic materials were extracted with CHCl\(_3\), and the combined organic layer was washed with brine. The organic layer was dried over anhydrous Na\(_2\)SO\(_4\), the drying agent filtered off, and the solvent evaporated. The organic material thus obtained was further purified with the silica gel column chromatography (hexane/CHCl\(_3\) as the eluent) to give brownish powdery 10 (346 mg, 36%) together with the starting 9 (527 mg, 52%).

\(\text{H NMR (300 MHz, CDCl}_3, \text{TMS): } \delta/\text{ppm} = 0.25 \text{ (9H, s), 0.88 (6H, t, J/Hz =7.2), 1.26 (32H, m), 1.49 (4H, m), 1.79 (4H, m), 3.93 (4H, m), 6.83 (1H, s), 7.25 (1H, s).}

\(\text{LRMS (EI, 70eV) } m/z \text{ (rel intensity/%) = 668 (M}^+\text{, 100).}

IR (neat) \text{ } \nu/\text{cm}^{-1} = 2957, 2920, 2848, 2160, 1485, 1467, 1372, 1250, 1213, 1162, 1032, 857, 841, 759, 722, 664, 640, 506, 490, 449, 439, 414.

Mp 38.0-40.9 °C.
Synthesis of 1,4-bis(dodecyloxy)-2-(4′-tert-butylphenylethynyl)-5-trimethylsilylethynylbenzene (11)

To a mixture of 10 (663 mg, 0.99 mmol), 4-tert-butylphenylacetylene (208 mg, 1.31 mmol, 1.3 eq), Pd(PPh3)2Cl2 (25.9 mg, 0.037 mmol, 0.04 eq) and CuI (8.1 mg, 0.043 mmol, 0.04 eq) in THF (10 mL) was added triethylamine (5 ml) in a two-necked flask, and the resulting solution was stirred at room temperature for overnight. The solvent was removed in vacuo, and 3 mol dm⁻³ aq. hydrochloric acid and CH₂Cl₂ were added. The organic materials were extracted with CH₂Cl₂, and the combined organic layer was washed with brine. The organic layer was dried over anhydrous Na₂SO₄, the drying agent filtered off, and the solvent evaporated. The organic material thus obtained was further purified with the silica gel column chromatography to give brownish powdery 11 (646 mg, 93%).

¹H NMR (300 MHz, CDCl₃, TMS): δ/ppm = 0.26 (9H, s), 0.88 (6H, m), 1.1-1.4 (41H, m), 1.52 (4H, m), 1.81 (4H, m), 3.98 (4H, m), 6.93 (1H, s), 6.95 (1H, s), 7.35 (2H, d, J/Hz = 8.7), 7.45 (2H, d, J/Hz = 8.7).

LRMS (EI, 70eV) m/z (rel intensity %) = 699 (M⁺, 100).

IR (neat) ν/cm⁻¹ = 2921, 2849, 2155, 1517, 1496, 1469, 1410, 1388, 1272, 1250, 1217, 1116, 1033, 891, 842, 759, 722, 639, 559, 537, 483, 405.

Mp 45.0-48.9 °C.

Synthesis of 1,4-bis(dodecyloxy)-2-(4′-tert-butylphenylenethynyl)-5-ethynylbenzene (12)

To a mixture of 11 (629 mg, 0.90 mmol) and K₂CO₃ (187 mg, 1.35 mmol, 1.5 eq) was added THF (13 mL) and CH₃OH (13 mL) and the resulting mixture was stirred at room temperature for overnight. To the solution was added hexane and sat. aq. NH₄Cl, and the organic material was extracted with hexane three times. The combined organic layer was dried over anhydrous Na₂SO₄, the drying agent filtered off, and the solvent evaporated. The organic material thus obtained was further purified with the silica gel column chromatography to give brownish powdery 12 (554 mg, 98%).

¹H NMR (300 MHz, CDCl₃, TMS): δ/ppm = 0.88 (6H, m), 1.2-1.4 (41H, m), 1.52 (4H, m), 1.82 (4H, m), 3.33 (1H, s), 3.99 (4H, m), 6.97 (1H, s), 6.98 (1H, s), 7.36 (2H, d, J/Hz = 8.7), 7.46 (2H, d, J/Hz = 8.7).

LRMS (EI, 70eV) m/z (rel intensity %) = 626 (M⁺, 100).

IR (neat) ν/cm⁻¹ = 3290, 2920, 2850, 2362, 1518, 1496, 1466, 1410, 1391, 1276, 1219, 1031, 1007, 876, 861, 830, 793, 723, 677, 655, 633, 559, 481, 458, 418, 404.

Mp 43.1-48.0 °C.

Synthesis of 1,4-bis(dodecyloxy)-2-(4′-tert-butylphenylenethynyl)-5-(4′′-phenylene)boronic acid (13)

To a solution of 12 (150 mg, 0.24 mmol), 4-iodophenylboronic acid (72 mg, 0.29 mmol, 1.2 eq), Pd(PPh₃)₄ (14.5 mg, 0.013 mmol, 0.05 eq), CuI (3.3 mg, 0.017 mmol, 0.07 eq) in THF (5 mL) was added diisopropylamine (5 mL) in a two-necked flask, and the resulting solution was stirred at room temperature for overnight. The solid material formed was filtered off, and the solvent was removed in vacuo. The organic material was extracted from the solid material obtained by CH₂Cl₂ several times, and the solvent of the combined organic layer was evaporated to give an orange powder. It was used for the next reactions without
further purification.

**Synthesis of 1o**

To a mixture of 14 [2] (50.2 mg, 0.070 mmol), 12 (96 mg, 0.15 mmol, 2.2 eq), Pd(PPh₃)₂Cl₂ (11.8 mg, 0.017 mmol, 0.24 eq) and CuI (11.1 mg, 0.058 mmol, 0.84 eq) in THF (6 mL) was added triethylamine (5 ml) in a two-necked flask, and the resulting solution was stirred at room temperature for 1.5 h. To the solution was added 3 mol dm⁻³ aq. hydrochloric acid and CH₂Cl₂. The organic materials were extracted with CH₂Cl₂ several times, and the combined organic layer was washed with brine. The organic layer was dried over anhydrous Na₂SO₄, the drying agent filtered off, and the solvent evaporated. The organic material thus obtained was further purified with the silica gel column chromatography to give 11 as a yellow oil (4.1 mg, 3.4%).

¹H NMR (300 MHz, CDCl₃, TMS): δ/ppm = 0.86 (12H, m), 1.2-1.4 (82H, m), 1.4-1.6 (8H, m), 1.85 (8H, m), 2.21, 2.49 (6H, s), 4.03 (8H, m), 6.97-7.01 (4H, m), 7.3-7.9 (14H, Aromatic protons).
MALDI-TOF MS (Reflectron mode) m/z = 1717 (M⁺).
IR (neat) ν/cm⁻¹ = 2923, 2853, 1496, 1464, 1414, 1381, 1340, 1269, 1215, 1147, 1113, 1046, 997, 964, 861, 833, 758, 735, 701, 560, 526, 489, 476, 463, 443, 426.

**Synthesis of 2o**

To a solution of 14 (50.3 mg, 0.070 mmol) and 12 (133 mg, 0.18 mmol, 2.6 eq) in THF (7 mL) in a two-necked flask was added aq. sat. K₂CO₃ (7 mL), Pd₂(dba)₃ (15.9 mg, 0.017 mmol, 0.25 eq) and tricyclohexylphosphine (2.1 mg, 0.0075 mmol, 0.11 eq), and the resulting solution was stirred at room temperature for overnight. To the solution was added 1 mol dm⁻³ aq. hydrochloric acid and CHCl₃. The organic materials were extracted with CHCl₃ several times, and the combined organic layer was washed with brine. The organic layer was dried over anhydrous Na₂SO₄, the drying agent filtered off, and the solvent evaporated. The organic material thus obtained was further purified with the silica gel column chromatography to give 2o as a yellow oil (10.0 mg, 7.7%).

¹H NMR (300 MHz, CDCl₃, TMS): δ/ppm = 0.86 (12H, m), 1.2-1.4 (82H, m), 1.4-1.6 (8H, m), 1.85 (8H, m), 2.26, 2.54 (6H, s), 4.04 (8H, m), 7.01, 7.03 (4H, s), 7.3-8.0 (22H, Aromatic protons).
MALDI-TOF MS (Reflectron mode) m/z = 1869 (M⁺).
IR (neat) ν/cm⁻¹ = 2921, 2852, 1518, 1494, 1465, 1414, 1380, 1339, 1269, 1214, 1193, 1146, 1112, 1091, 1047, 1030, 993, 966, 834, 815, 758, 721, 561, 529, 476, 457, 447, 439, 418.

**Synthesis of 3o**

A solution of 15 [3] (50.5 mg, 0.064 mmol), 13 (82.3 mg, 0.13 mmol, 2.0 eq), Pd(PPh₃)₄ (6.0 mg, 0.0052 mmol, 0.081 eq) and Ag₂O (24.9 mg, 0.11 mmol, 1.7 eq) in THF (6 mL) in a vial for the microwave heating apparatus was heated at 80 °C for 15 min. Insoluble materials were filtered off through Celite, and the solvent of the filtrate was removed in vacuo. The organic material thus obtained was further purified with the silica gel column chromatography to give 3o as a brown amorphous solid (64.8 mg, 56.5%).

¹H NMR (300 MHz, CDCl₃, TMS): δ/ppm = 0.87 (12H, t, J/Hz = 7.2), 1.2-1.4 (82H, m), 1.4-1.6 (8H, m), 1.84
(8H, m), 2.06, 2.22 (6H, s), 4.02 (8H, m), 6.9-7.2 (6H, m), 7.3-7.9 (12H, Aromatic protons).
MALDI-TOF MS (Reflectron mode) m/z = 1781 (M').
IR (neat) v/cm⁻¹ = 2921, 2852, 1496, 1467, 1416, 1321, 1276, 1216, 1173, 1153, 1132, 1115, 1042, 1018, 952, 834, 722, 571, 495, 478, 462, 431, 421.

Synthesis of 4o.
To a solution of 15 (30.3 mg, 0.039 mmol) and 13 (73 mg, 0.098 mmol, 2.5 eq) in THF (5 mL) in a two-necked flask was added aq. sat. K₂CO₃ (5 mL), Pd₂(dba)₃ (7.8 mg, 0.0085 mmol, 0.22 eq) and tricyclohexylphosphine (1.2 mg, 0.0043 mmol, 0.11 eq), and the resulting solution was stirred at room temperature for 2 h 40 min. To the solution was added 0.5 mol dm⁻³ aq. hydrochloric acid and CHCl₃. The organic materials were extracted with CHCl₃ several times, and the combined organic layer was washed with brine. The organic layer was dried over anhydrous Na₂SO₄, the drying agent filtered off, and the solvent evaporated. The organic material thus obtained was further purified with the silica gel column chromatography to give 4o as an orange oil (5.1 mg, 6.8%).

1H NMR (300 MHz, CDCl₃, TMS): δ/ppm = 0.86 (12H, m), 1.2-1.4 (82H, m), 1.4-1.6 (8H, m), 1.85 (8H, m), 2.11, 2.25 (6H, s), 4.03 (8H, m), 7.03 (4H, m), 7.2~8.0 (22H, Aromatic protons).
MALDI-TOF MS (Reflectron mode) m/z = 1933 (M').
IR (neat) v/cm⁻¹ = 2923, 2852, 1519, 1495, 1469, 1415, 1318, 1277, 1216, 1173, 1153, 1129, 1113, 1060, 1043, 1015, 957, 833, 721, 687, 562, 489, 478, 468, 448.

Synthesis of 6.
To a mixture of 4,9-bis(4-iodophenyl)diamantane 16 [4] (98.4 mg, 0.166 mmol), Pd(PPh₃)₄ (21.9 mg, 0.019 mmol, 0.11 eq) and CuI (6.4 mg, 0.034 mmol, 0.20 eq) in a three-necked flask was added piperidine (10 mL), and the resulting mixture was heated up to 60 °C. When THF (5 mL) was added to the mixture, the content became a clear solution. To it was added a solution of 13 (209 mg, 0.333 mmol, 2.0 eq) in piperidine (6 mL) dropwise. After the solution was heated at 60-70 °C for 4 h, it was stirred for overnight at room temperature. After the solvent was removed from the reaction flask in vacuo, 3 mol dm⁻³ aq. hydrochloric acid and CH₂Cl₂ was added and the organic materials were extracted with CH₂Cl₂ several times. The combined organic layer was washed with brine, dried over anhydrous Na₂SO₄, the drying agent filtered off, and the solvent evaporated. The organic material thus obtained was further purified with the silica gel column chromatography (hexane/CHCl₃ as the eluent) to give 6 as a yellow powder (75.4 mg, 29%).

1H NMR (300 MHz, CDCl₃, TMS): δ/ppm = 0.88 (12H, t, J/Hz = 7.2), 1.2-1.4 (82H, m), 1.5-1.6 (8H, m), 1.85 (8H, m), 1.98 (18H), 4.03 (8H, t, J/Hz = 6.4), 7.01 (4H, s), 7.36 (4H, d, J/Hz = 8.3), 7.39 (4H, d, J/Hz = 8.7), 7.48 (4H, d, J/Hz = 8.9), 7.50 (4H, d, J/Hz = 9.8).
MALDI-TOF MS (Reflectron mode) m/z = 1592 (M').
IR (neat) v/cm⁻¹ = 2919, 2849, 1516, 1492, 1466, 1415, 1377, 1267, 1212, 1017, 867, 833, 797, 722, 706, 665, 560, 465.
Mp 134.0-137.0 °C
References

3. $^1$H NMR spectra

300 MHz in CDCl$_3$ with TMS as the internal standard

$^1$H NMR spectrum of 1o

300 MHz, CDCl$_3$
1H NMR spectrum of 20

300 MHz, CDCl₃
$^1$H NMR spectrum of 3o
300 MHz, CDCl$_3$
1H NMR spectrum of 40
300 MHz, CDCl3
1H NMR spectrum of 6
300 MHz, CDCl₃

| 7.52064 | 7.49177 | 7.48800 | 7.45913 | 7.40013 | 7.37879 | 7.37126 | 7.35117 | 7.26079 | 7.00722 | 4.04967 | 4.02833 | 4.00699 | 1.97839 | 1.88926 | 1.86667 | 1.84407 | 1.81771 | 1.79637 | 1.55911 | 1.51769 | 1.49635 | 1.33064 | 1.25658 | 0.89881 | 0.87747 | 0.85362 | 0.01130 | 0.00000 | -0.01004 | 7.5 | 7.4 | 7.3 | 8.10 | 8.05 | 3.95 | 8.00 | 17.58 | 8.39 | 18.67 | 86.04 | 12.63 |
MALDI-TOF mass spectra

%Int.  8.0 mV[sum= 974 mV] Profiles 1-121 Unsmoothened

Mass/Charge

1700 1710 1720 1730 1740 1750 1760 1770 1780 1790 1800
%Int.  3.3 mV [sum= 329 mV] Profiles 1-100 Unsmoothed
%Int. 557 mV [sum = 111317 mV] Profiles 1-200 Unsmoothed
5. Frontier orbitals of DFT-optimized structures of 1o/1c, 2o/2c, 3o/3c and 4o/4c

ESI-Fig. 1. Frontier orbitals of (a) 1o and (b) 1c
ESI-Fig. 1 (continued). Frontier orbitals of (c) 2o and (d) 2c
ESI-Fig. 1 (continued). Frontier orbitals of (e) 3o and (f) 3c.
ESI-Fig. 1 (continued). Frontier orbitals of (g) 4o and (h) 4c
6. Fluorescence spectra of 1o and its photostationary state of 313-nm light irradiation

ESI-Fig. 2. Fluorescence spectra of (a) 1o and (b) its photostationary state of 313-nm light irradiation.
Concentration: 1.15 x 10^-6 mol dm^-3 in toluene. Excitation: 372 nm (red) and 440 nm (blue).
7. Absorption spectral change of 2o by 313-nm light irradiation in toluene

![Absorption spectral change of 2o by 313-nm light irradiation in toluene](image)

**ESI-Fig. 3.** Absorption spectral change of 2o by UV irradiation in toluene.
Concentration: $4.14 \times 10^{-5}$ mol dm$^{-3}$. Irradiation: 313 nm, 0.29 mW cm$^{-2}$.

8. Fluorescence spectral change of 2o by 313-nm light irradiation in toluene

![Fluorescence spectral change of 2o by 313-nm light irradiation in toluene](image)

**ESI-Fig. 4.** Fluorescence spectral change of 2o by UV irradiation in toluene.
Concentration: $1.66 \times 10^{-6}$ mol dm$^{-3}$. Irradiation: 313 nm, 0.29 mW cm$^{-2}$. Excitation: 372 nm.
9. Absorption and fluorescence spectra of model compound 6 in toluene

ESI-Fig. 5. Absorption spectrum and fluorescence spectrum of 6 in toluene.
10. Absorption spectral change of 4o by UV and visible light irradiation in toluene

**ESI-Fig. 6.** Absorption spectral change of 4o by UV and vis light irradiation in toluene.

Concentration: $3.00 \times 10^{-5}$ mol dm$^{-3}$. (a) Irradiation: 313 nm, 0.31 mW cm$^{-2}$. (b) 506 nm to the resultant solution of (a), 3.0 mW cm$^{-2}$, 0 – 2 min; >490 nm, 50 mW cm$^{-2}$, 2 – 2.5 min; >490 nm, 100 mW cm$^{-2}$, 2.5 – 3 min: >490 nm, 800 mW cm$^{-2}$, 3 – 73.5 min.
11. Fluorescence spectral change of 4o by 313-nm light irradiation in toluene

ESI-Fig. 7. Spectral fluorescence change of 4o by UV irradiation in toluene. Concentration: 1.20 x 10^{-6} mol dm^{-3}. Irradiation: 313 nm, 0.30 mW cm^{-2}. Excitation: 495 nm.

12. Absorption spectral properties obtained by TD DFT calculations of 1o

ESI-Table 1. Absorption spectral properties obtained by TD DFT calculations of 1o

<table>
<thead>
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<th>( \lambda_{\text{max}} ), nm</th>
<th>Strength</th>
<th>MO Component</th>
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<td>0.083</td>
<td>HOMO-1 to LUMO+2</td>
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<tr>
<td>397</td>
<td>0.004</td>
<td>HOMO to LUMO+2</td>
<td>58%</td>
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<td></td>
<td></td>
<td>HOMO-1 to LUMO</td>
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<td></td>
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<td>405</td>
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<td>HOMO-1 to LUMO</td>
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<td>HOMO to LUMO+2</td>
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<td></td>
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<td>HOMO to LUMO</td>
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\( a \) HOMO-1: -5.1 eV; HOMO: -5.1 eV; LUMO: -1.8 eV; LUMO+1: -1.8 eV.
13. Absorption spectral properties obtained by TD DFT calculations of 2o

**ESI-Table 2.** Absorption spectral properties obtained by TD DFT calculations of 2o<sup>a</sup>

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<th>%</th>
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<td>HOMO-1 to LUMO+1</td>
<td>17%</td>
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<td>379</td>
<td>0.002</td>
<td>HOMO-1 to LUMO+1</td>
<td>82%</td>
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<tr>
<td>388</td>
<td>0.161</td>
<td>HOMO to LUMO+2</td>
<td>79%</td>
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<td>391</td>
<td>1.449</td>
<td>HOMO-1 to LUMO</td>
<td>72%</td>
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<tr>
<td>401</td>
<td>0.013</td>
<td>HOMO to LUMO</td>
<td>98%</td>
</tr>
</tbody>
</table>

<sup>a</sup> HOMO-1: -5.2 eV; HOMO: -5.1 eV; LUMO: -1.8 eV; LUMO+1: -1.8 eV.