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Benzo[1,2,5]selenadiazole bridged amines: electro-optical properties

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Abstract—New diamines and tetramines bridged by a low band gap rendering chromophore benzo[1,2,5]selenadiazole were synthesized by following palladium-catalyzed methodologies developed by Hartwig, Stille, or Suzuki. These donor–acceptor compounds display unique absorption and emission characteristics, which are dependent on the strength of the donors.

Donor–acceptor–donor (D–A–D) type π-conjugated molecules have attracted much attention recently due to their characteristic electronic and optical properties.[1] This type of semiconducting materials have been demonstrated utility in device applications ranging from light-emitting diodes,[2] photovoltaic cells,[3] field-effect transistors,[4] and nonlinear optics.[5]

Syntheses of selenium containing compounds and the further utilization of these compounds in organic synthesis have steadily increased.[6] Although wide variety of thiadiazole containing compounds are known, only limited selenadiazole containing compounds have been prepared.[7] Selenium atom has a much larger size and less electronegativity than the sulfur atom; it would have a more important influence on the electro-optical properties of the small molecules. In this context, selenium containing compounds are of much interest. In addition, it is also expected that benzo[1,2,5]-selenadiazole conjugation will lead to red-shift in optical spectra when compared to the sulfur analogue benzo[1,2,5]thiadiazole.

Benzo[1,2,5]thiadiazole-based small molecules have been shown to possess interesting electro-optical properties such as two-photon absorption[8] characteristics and applied in devices including liquid crystal displays (LCDs),[9] organic light-emitting diodes (OLEDs),[10] photovoltaic cells,[11] and thin film transistors.[12] Their charge transport capability and color purity make them attractive candidates for OLED applications. Few examples of electroluminescent applications have been reported recently for benzo[1,2,5]selenadiazole-based co-polymers.[13] However, small molecules incorporating benzo[1,2,5]senenadiazole are scarce. In this letter, we report a series of diamines and a tetramine containing benzo[1,2,5]selenadiazole bridge and thienyl or phenylene conjugation. To the best of our knowledge, selenadiazole bridged amines are not reported yet. For comparison, we have synthesized an unaminated version (**S1**) also.

The dipolar benzo[1,2,5]selenadiazole compounds were conveniently prepared according to Scheme 1. Compounds **S1** and **S2** were synthesized from 4,7-dibromobenzo[1,2,5]selenadiazole either treating with *p-tert*-butylbenzene boronic acid or *N*,*N*-diphenyl-4-aminophenylboronic acid and following Suzuki protocol. Compounds **S3**, **S4**, and **S5** were obtained by Stille coupling reactions involving 4,7-dibromobenzo[1,2,5]selenadiazole and the corresponding stannylene derivatives. Compound **S6** was obtained in excellent yield by the palladium-catalyzed C–N coupling strategy developed by Hartwig and co-authors. All the new compounds were characterized by ^{1}H and ^{13}C NMR spectra, FAB mass spectra, and elemental analysis.[14] The structures of compounds **S1** and **S6** were further confirmed by single crystal X-ray diffraction analysis.[15] The molecular structures of **S1** and **S6** are depicted in Figures 1 and 2, respectively. In the structure of **S1**, there are two molecules in the asymmetric unit and they display close contact between the Se1 and N3 atoms (2.977 Å). Similarly, Se–N short intermolecular interactions were also noticed for **S6**.

Keywords: Benzoselenadiazole; Electro-optics; Amines; Donor–acceptor compounds; Photophysical properties.

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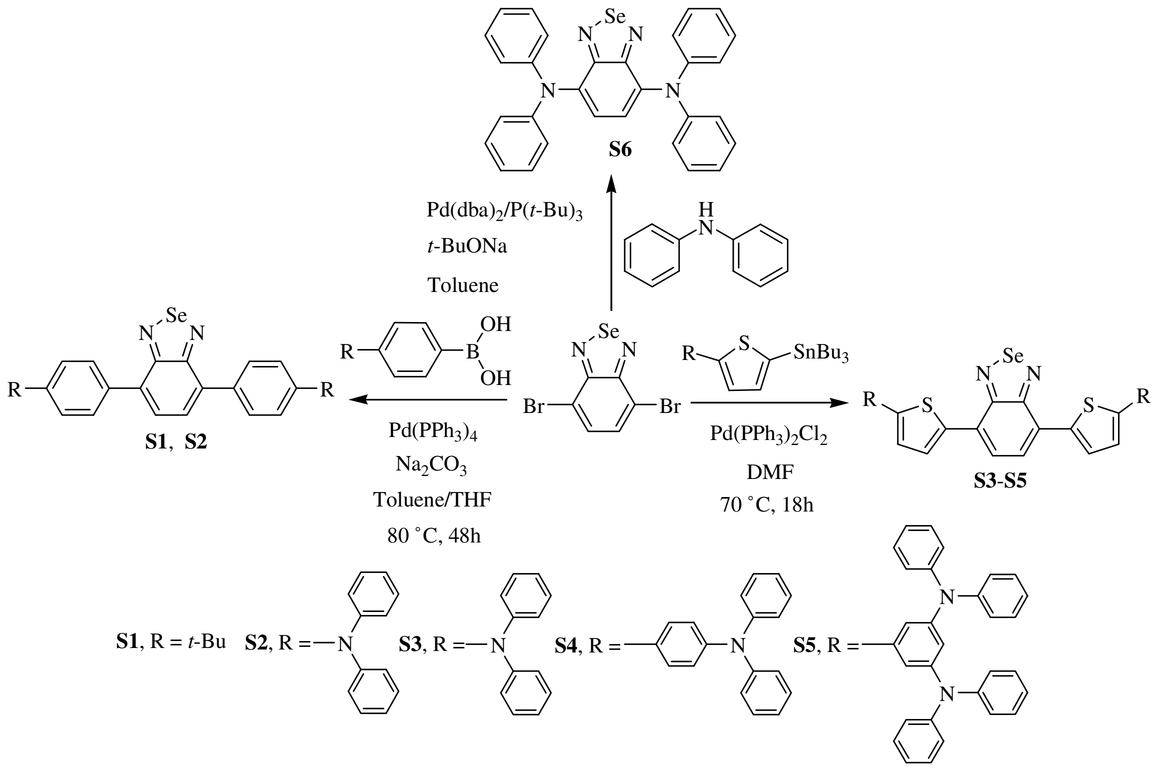

Scheme 1. Synthesis of the compounds.

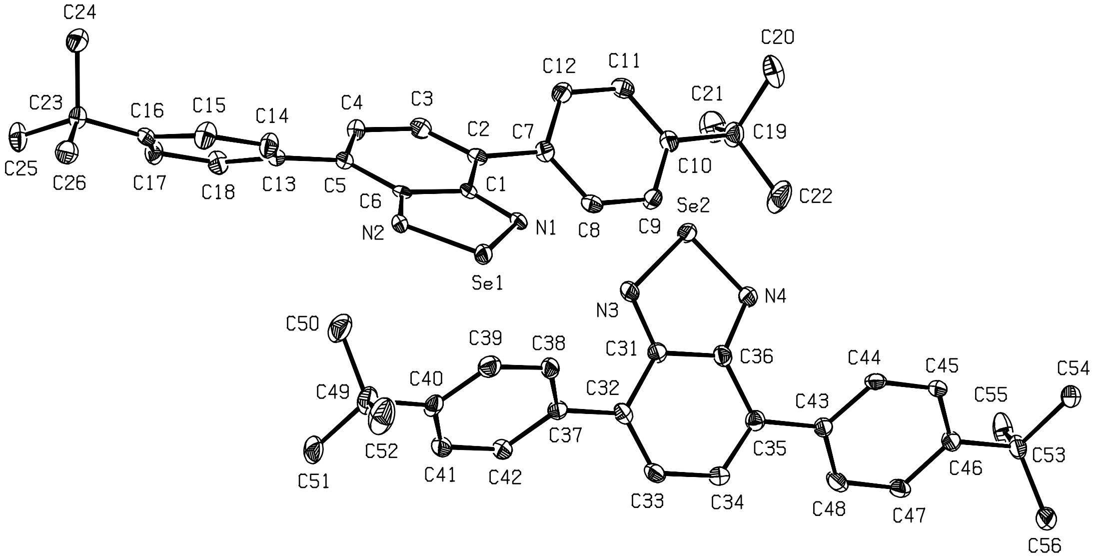

Figure 1. Molecular structure of **S1**.

The electronic absorption spectra of the compounds measured in dichloromethane possess two prominent bands arising from π→π* and charge-transfer (CT) transitions (Table 1 and Fig. 3). Additional shoulders in the lower wavelength region are also visible for the molecules that are ascribed to the n→π* transitions. The low energy absorption wavelength (λ_{abs}) attributable to the CT transition increases in the order of **S1** < **S2** < **S5** < **S6** < **S4** < **S3** and is consistent with the electron-donating strength of the capping segments. In compound **S5**, the *meta* displacement of diphenylamino moieties effectively deconjugates them from the aromatic core, which leads to a blue shift in the CT band when compared to that of **S4**. The absorption maxima of **S1**, **S2**, **S4**, and **S5** are observed in a longer wavelength (389, 459, 529, and 489 nm, respectively) region when compared to that of the corresponding benzo[1,2,5]thiadiazole analogs.[10b] This leads to comparatively small HOMO–LUMO gap than the benzothiadiazole derivatives. The donor strength of the capping segments is also manifested on the fluorescence profile of the compounds leading to a similar trend in emission

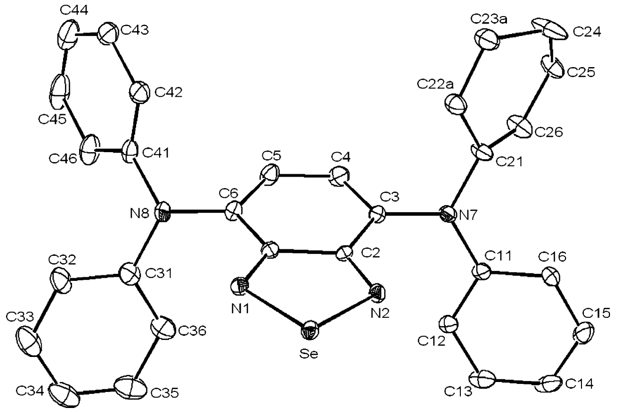

Figure 2. ORTEP diagram of the molecule **S6**.

maxima (**S1** < **S2** < **S5** < **S6** < **S4** < **S3**). See Figure 3 for representative examples. The most red-shifted emission peak observed for compounds **S3**, **S4**, and/or **S6** is attributed to the elongated conjugation and enhanced donor–acceptor interaction. Also, the diminished photoluminescence efficiency observed for compounds **S3** and **S6** are probably due to the reductive quenching and pronounced dipolar interactions, respectively. These speculations are reasonable as compound **S3** possesses the least positive oxidation potential in the series (vide infra) and compound **S6** contains two diamines directly tethered to the electron-withdrawing benzoselenadiazole unit.

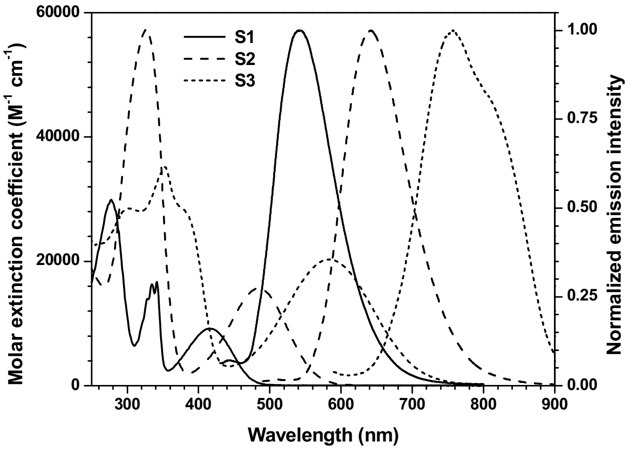

Figure 3. Absorption and emission spectra of the compounds **S1**, **S2**, and **S3** recorded in dichloromethane and toluene, respectively.

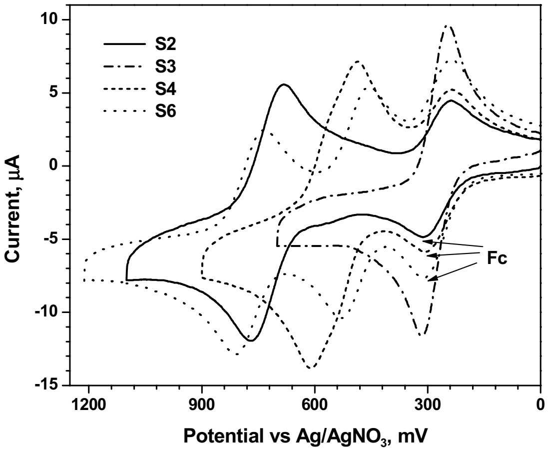

Figure 4. Cyclic voltammograms of **S2**, **S3**, **S4**, and **S6** (2.5×10^{-4} M) in dichloromethane (0.1 M Bu_4NPF_6) at a glassy carbon working electrode with scan rate = 100 mV s^{-1} under a N_2 atmosphere. Only the amine oxidation is displayed.

The redox propensity of the compounds were investigated by cyclic voltammetry in dichloromethane solutions. All the compounds display a reduction couple arising from the benzoselenadiazole moiety. This reduction wave shifts positively for compounds **S3**, **S4**, and **S5** on insertion of the thiophene segments on the conjugation bridge. This points that the reduction in **S3**, **S4**, and **S5** originates from the dithienylbenzoselenadiazole low band gap chromophore while in the other compounds it originates from the benzoselenadiazole segment. A similar observation was made earlier for the benzothiadiazole derivatives.[10b,16] On the other hand, the donor groups do not affect the reduction potential significantly (compare **S1** with **S2** and **S6**). The reduction potentials observed for this class of compounds are more positive than that of the corresponding benzothiadiazole analogs.[10b] This indicates that the benzoselenadiazole moiety is more electron deficient than the benzothiadiazole nucleus.[13] Also, all the compounds show an oxidation couple originating either from the π-conjugated aromatic segment or end-capping amino units (Fig. 4). Interestingly, the two amino groups in compound **S6** led to two separate one-electron reversible

Table 1. Physical properties of the compounds

Compd	λ_{abs}, nm[a]	λ_{em}, nm (Φ_f, %)[b]	$T_g/T_m/T_d$, °C[c]	$E_{1/2}$ (ΔE_p), V[d]	HOMO, eV	LUMO, eV	ΔE, eV
S1	414, 341, 277	562 (68)	na/242/272	1.076 (96), −1.839 (82)	5.876	2.961	2.915
S2	484, 326	644 (41)	100/277/405	0.437 (101), −1.822 (88)	5.238	2.978	2.260
S3	584, 352, 298	775 (3)	73/186/406	0.001 (76), −1.628 (85)	4.801	3.172	1.629
S4	562, 381, 306	728 (21)	125/264/451	0.272 (137), 0.850 (89), −1.598 (78)	5.072	3.202	1.870
S5	529, 354, 306	667 (54)	141/297/460	0.479 (134), 0.842 (151), −1.623 (87)	5.279	3.177	2.102
S6	544, 345, 296	721 (2)	na/238/290	0.217 (77), 0.494 (77), −1.805 (82)	5.017	2.996	2.021

[a] Measured for dichloromethane solutions.

[b] Measured for toluene solutions. DCM ($\Phi_f = 0.45$ in acetonitrile) was used as a standard for the quantum yield measurements.

[c] Measured under a flow of nitrogen with a scan rate of 10°/min. T_d is quoted as the temperature corresponding to 5% weight loss.

[d] Data were from the cyclic voltammograms recorded using glassy carbon working electrode, non-aqueous Ag/AgNO$_3$ reference electrode, Bu_4NPF_6 as electrolyte and a scan rate of 100 mV/s.

oxidation couples indicating the electronic communication between the redox units through the short conjugation bridge. Longer linker in **S2**, **S3**, **S4**, and **S5** led to a single overlapping two-electron oxidation couple. The electron-rich thienyl unit significantly lowers the oxidation potential of the amines in **S3** and **S4** when compared to **S2**. The strong electronic interaction between the two diarylamines significantly lowers the first oxidation potential of **S6**. Consequently, the first oxidation potential of **S6** is smaller than that of **S2**. An additional oxidation wave observed for compounds **S4** and **S5** is attributed to the conjugation segment.

The thermal stability and the amorphous nature of the compounds were investigated by thermogravimetry (TGA) and differential scanning calorimetry (DSC), respectively. Except for **S1** and **S6**, all the compounds exhibited a glass transition temperature (T_g) after fast cooling from the melt. The T_g values are comparable to the commonly used hole-transporting materials. Particularly, the T_g value observed for compound **S5** is larger than that of the routinely used electroluminescent materials.[17] The high value observed for **S5** is attributed to the higher molecular mass and the presence of starburst molecular architecture. On the contrary, compound **S2** has lower T_g than **S3** even though the two have nearly same number of non-hydrogen atoms and molecular weights. The difference possibly stems from the facile rotations of the thienyl unit in **S2** than the phenyl unit in **S3** due to the less steric congestion in the former.

In summary, we have synthesized new class of donor–acceptor compounds featuring benzoselenadiazole electron-accepting units as the central bridge. These dipolar compounds display distinct optical, electrochemical, and thermal properties. Additionally, we also unravel that the benzoselenadiazole unit is more electron deficient than the benzothiadiazole unit. They are potential candidates for two-photon absorption, nonlinear optics, and electroluminescent applications. Particularly, we believe that the near-infrared emitting compounds **S3**, **S4**, and **S6** may be suitably exploited for optical communication, medical and biological, and sensor applications.[18] Work towards these directions is underway.

Acknowledgements

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14. Compounds **S1** and **S2** were synthesized from 4,7-dibromobenzo[1,2,5]selenadiazole with *p*-*tert*-butylbenzene boronic acid and *N*,*N*-diphenyl-4-aminophenylboronic acid, respectively, by Suzuki coupling reactions. Only the preparation of **S1** will be described in detail.
    To a stirred solution of 4,7-dibromobenzo[1,2,5]selenadiazole (1.7 g, 5 mmol), *p*-*tert*-butylbenzeneboronic acid (2.13 g, 12 mmol), $Pd(PPh_3)_4$ (0.15 g, 0.15 mmol) and Na_2CO_3 (1.47 g, 10 mmol) in toluene (10 mL), THF (10 mL) and H_2O (2 mL) was heated at reflux under N_2 atmosphere for 24 h. When the reaction was completed,

water was added to quench the reaction. The product was extracted with diethyl ether. The organic layer was collected, dried over anhydrous $MgSO_4$, and evaporated under vacuum. The crude product **S1** was purified by column chromatography on silica gel, using CH_2Cl_2/hexane mixture as eluent to give a yellow solid. Yield: 80%. FAB MS (*m*/*z*): 448.08 (M^+), ^{1}H NMR (δ, $CDCl_3$): 1.37 (s, 18H), 7.53–7.59 (m, 4H), 7.59 (s, 2H), 7.78–7.81 (m, 4H), ^{13}C NMR (δ, $CDCl_3$): 159.8, 151.1, 135.1, 134.7, 129.0, 128.2, 125.4, 34.6, 31.3. Elemental analysis calculated (%) for $C_{26}H_{28}N_2Se$: C, 69.79; H, 6.31; N, 6.26 Found: C, 70.24; H, 6.23; N, 6.25.

Selected data: **S2**. Red solid, yield 65%. FAB MS (*m*/*z*): 670 (M^+), ^{1}H NMR (δ, $CDCl_3$): 7.02 (t, $J = 7.2$ Hz, 4H), 7.15–7.19 (m, 12H), 7.25–7.29 (m, 8H), 7.57 (s, 2H), 7.76–7.78 (m, 4H), ^{13}C NMR (δ, $CDCl_3$): 159.8, 147.8, 147.5, 133.9, 131.6, 130.1, 129.3, 127.8, 124.8, 123.2, 122.8. Elemental analysis calculated (%) for $C_{42}H_{30}N_4Se$: C, 75.33; H, 4.52; N, 8.37. Found: C, 75.50; H, 4.58; N, 8.08.

Compounds **S3**, **S4**, and **S5** were synthesized from 4,7-dibromobenzo[1,2,5]selenadiazole with diphenyl-(5-tributylstannanyl-thiophen-2-yl)-amine, diphenyl-[4-(5-tributylstannanyl-thiophen-2-yl)-phenyl]-amine and *N*,*N*,*N*′,*N*′-tetraphenyl-5-(5-tributylstannanyl-thiophen-2-yl)-benzene-1,3-diamine, respectively, by Stille coupling reactions.

S3. 4,7-Dibromobenzo[1,2,5]selenadiazole (1.70 g, 5 mmol) diphenyl-(5-tributylstannanyl-thiophen-2-yl)-amine (5.4 g, 10 mmol) and $Pd(PPh_3)_2Cl_2$ (140 mg) were charged in a 250 mL round-bottomed flask. Under a nitrogen atmosphere, 15 mL DMF was added and the contents were heated to 80 °C and maintained at this temperature for 24 h. After the reaction was complete, the reaction mixture was diluted with methanol. The precipitate obtained was filtered and washed with methanol, and dried. The residue was adsorbed on silica gel and purified by column chromatography using dichloromethane/hexane mixture as eluent to give dark blue solid, yield 75%. FAB MS (*m*/*z*): 682.1 (M^+), ^{1}H NMR (δ, $CDCl_3$): 6.72 (d, $J =$ 4.0 Hz, 2H), 7.09–7.11 (m, 4H), 7.20–7.23 (m, 8H), 7.34–7.38 (m, 8H), 7.82 (s, 2H), 7.95 (d, $J = 4.0$ Hz, 2H). Elemental analysis calculated (%) for $C_{38}H_{26}N_4S_2Se$: C, 66.95; H, 3.84; N, 8.22. Found: C, 66.59; H, 3.78; N, 8.01.

S4. Red solid, yield 70%. FAB MS (*m*/*z*): 833.9 (M^+). ^{1}H NMR (δ, $CDCl_3$): 7.04–7.16 (m, 16H), 7.27–7.31 (m, 10H), 7.56–7.58 (d, $J = 7.8$ Hz, 4H), 7.79 (s, 2H), 8.01 (d, $J = 4$ Hz, 2H), ^{13}C NMR (δ, $CDCl_3$): 158.31, 147.6, 147.5, 145.8, 138.3, 129.4, 128.6, 128.3, 127.2, 126.7, 125.4, 124.7, 123.6, 123.3, 123.0. Elemental analysis calculated (%) for $C_{50}H_{34}N_4S_2Se$: C, 72.01; H, 4.11; N, 6.72. Found: C, 71.78; H, 4.07; N, 6.64.

S5. Red solid, yield 65%. FAB MS (*m*/*z*): 1169.3 ($M+H^+$). ^{1}H NMR (δ, $CDCl_3$): 6.77 (t, $J = 1.8$ Hz, 2H), 6.98–7.03 (m, 12H), 7.11–7.14 (m, 18H), 7.22–7.27 (m, 16H), 7.67 (s, 2H), 7.88 (d, $J = 4.0$ Hz, 2H), ^{13}C NMR (δ, $CDCl_3$): 115.8, 119.2, 122.9, 123.0, 124.24, 124.26, 124.30, 124.34, 124.36, 124.38, 124.40, 125.6, 127.2, 128.4, 129.3, 136.11, 139.18, 145.5, 147.4, 149.2, 158.1. Elemental analysis calculated (%) for $C_{74}H_{52}N_6S_2Se$: C, 76.07; H, 4.49; N, 7.19. Found: C, 75.94; H, 4.23; N, 6.99.

S6. A mixture of 4,7-dibromobenzo[1,2,5]selenadiazole (0.68 g, 2 mmol), diphenylamine (0.67 g, 4.4 mmol), sodium *tert*-butoxide (0.576 g, 6.0 mmol), $Pd(dba)_2$ (24 mg, 0.04 mmol), $P(t\text{-}Bu)_3$ (12 mg, 0.06 mmol), and toluene (25 mL) was heated to 80 °C under nitrogen atmosphere and stirred for 8 h. After it cooled, the solution was poured into water and extracted with diethyl ether. The crude product obtained by evaporation of the volatiles was purified by column chromatography. The desired compound was eluted with hexane/dichloromethane (3:2) mixture. Red solid, Yield 70%. FAB MS (*m*/*z*): 519.1 ($M+H^+$). ^{1}H NMR (δ, $CDCl_3$): 6.99–7.07 (m, 16H), 7.22–7.26 (m, 6H). ^{13}C NMR (δ, $CDCl_3$): 158.2, 148.0, 137.6, 129.3, 125.5, 123.6, 123.0. Elemental analysis calculated (%) for $C_{30}H_{22}N_4S_2$: C, 69.63; H, 4.29; N, 10.83. Found: C, 69.55; H, 4.08; N, 10.78.

15. Crystal data for **S1**: $C_{26}H_{28}N_2Se$, $M = 447.46$, triclinic, P-1, $a = 11.242(4)$ Å, $b = 13.927(6)$ Å, $c = 14.287(4)$ Å, $\alpha = 96.165(13)°$, $\beta = 98.445(12)°$, $\gamma = 93.193(13)°$, $V = 2194.1(14)$ Å^3, $Z = 4$, $D_e = 1.355$ Mg/m^3, μ (Mo-K$_\alpha$) = 1.726 mm^{-1}, $F(000) = 928$, yellow green crystal, size: $0.18 \times 0.14 \times 0.04$ mm^3, 7650 reflections measured (7650 unique), $R_w = 0.0617$ for all data, $R = 0.0359$, $wR2 = 0.0800$ for 5723 on *F*-values of reflections with $I > 2\sigma(I)$, $S = 1.119$ for all data and 524 parameters. Crystal data for **S6**: $C_{33}H_{35}N_4Se$, $M = 558.55$, monoclinic, $P2_1/c$, $a = 17.8066(13)$ Å, $b = 9.5872(7)$ Å, $c = 15.9520(12)$ Å, $\beta = 90.644(3)°$, $V = 2723.1(3)$ Å^3, $Z = 4$, $D_e = 1.362$ Mg/m^3, μ (Mo-K$_\alpha$) = 1.408 mm^{-1}, $F(000) =$ 1148, red prism, size: $0.22 \times 0.18 \times 0.08$ mm^3, 6607 reflections measured (4817 unique), $R_w = 0.0518$ for all data, $R = 0.0380$, $wR2 = 0.0815$ for 3894 on *F*-values of reflections with $I > 2\sigma(I)$, $S = 1.092$ for all data and 362 parameters. Unit cell determination and intensity data collection ($2\theta = 50°$) were performed on a Bruker smart APEX CCD diffractometer at 100 (2) K. The structure was solved by direct methods and refinements were made by full-matrix least-squares methods on F^2. Programs: Bruker X8APEX was used for data collection and cell refinement, Bruker SAINT was used for data processing, SHELXS-97 was used for structure determination, SHELXL-97 was used for refinements, Ortep-3 for molecular graphics. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 277591 and CCDC 277620. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44(0)-1233-336033 or e-mail: deposit@ccdc.cam.ac.uk].

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