Synthesis, stability and bonding situation of tris-, bis- and mono[9-(azuleno[1,2-*b*]thienyl)]methyl cations

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Electronic supplementary information (ESI)

CV waves of compounds **7a**, **8a** and **9a**, redox details of compounds **7a**,**b**, **8a**,**b** and **9a**,**b** along with those of **4a**, **5a** and **6a**, ORTEP drawings and details of the X-ray analysis of compounds **2b** and **9b** and NMR details of compounds reported.

CV waves of compounds 7a, 8a and 9a, redox details of compounds 7a,b, 8a,b and 9a,b along with those of 4a, 5a and 6a

Table S-1. Redox potentials of **7a**,**b**, **8a**,**b**, **9a**,**b**, **4a**, **5a** and **6a**

Cation	E_1^{red}	E_2^{red}	E_3^{red}	E_4^{red}	E_1^{ox}	E_2^{ox}	E_3^{ox}	Ref.
7a	(–0.75)	(–1.25)	(–1.67)	(–1.88)	+0.81	+0.91	(+1.42)	
7b	–0.81	(–1.51)	(–1.72)	(–2.00)	+0.75	+0.87	(+1.44)	
8a	(–0.67)	(–1.42)	(–1.63)	(–1.75)	+0.85	(+1.37)		
8b	(–0.72)	(–1.26)	(–1.49)	(–1.78)	+0.82	(+1.37)		
9a	(–0.53)	(–0.61)	(–1.86)	(–2.07)	(+1.49)			
9b	(–0.58)	(–1.49)	(–1.64)	(–1.92)	(+1.51)			
4a	–0.78	(–1.56)			(+0.98)	(+1.07)		9d
5a	–0.66	(–1.52)			(+1.04)	-		9d
6a	(–0.48)	-			(+1.41)	-		9d

The redox potentials were measured by CV or DPV (0.1 M Et_4NClO_4 in MeCN, Pt electrode, scan rate 100 mV s^{-1}, and Fc/Fc^+ = 0.08 V). In the case of irreversible waves, which are shown in parentheses, E_{ox} and E_{red} were calculated as E_{pa} (anodic peak potential) – 0.03 and E_{pc} (cathodic peak potential) + 0.03 V, respectively.

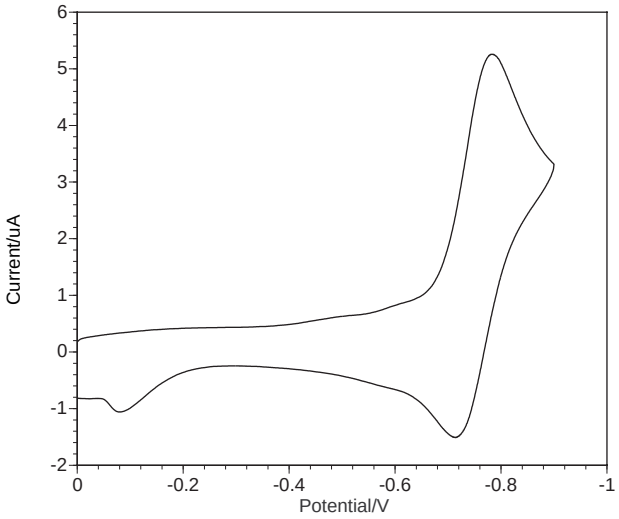

Figure S-1. Reduction wave of **7a** in acetonitrile containing Et_4NBF_4 (0.1 M) as a supporting electrolyte.

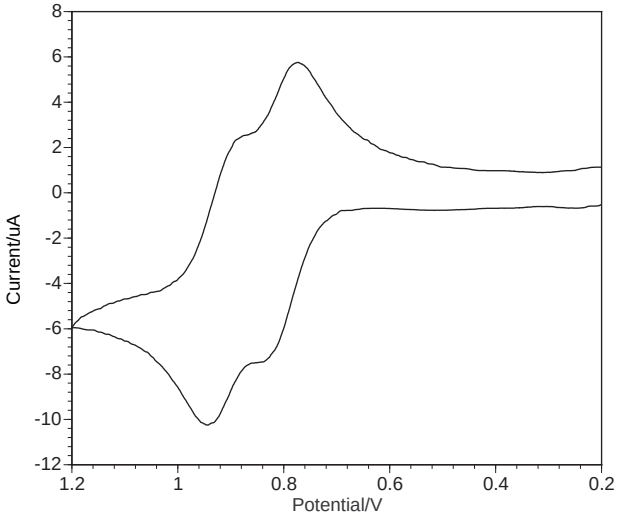

Figure S-2. Oxidation wave of **7a** in acetonitrile containing Et_4NBF_4 (0.1 M) as a supporting electrolyte.

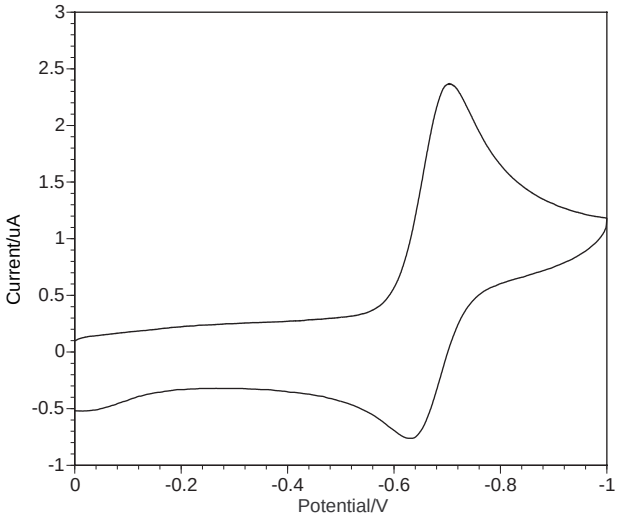

Figure S-3. Reduction wave of **8a** in acetonitrile containing Et_4NBF_4 (0.1 M) as a supporting electrolyte.

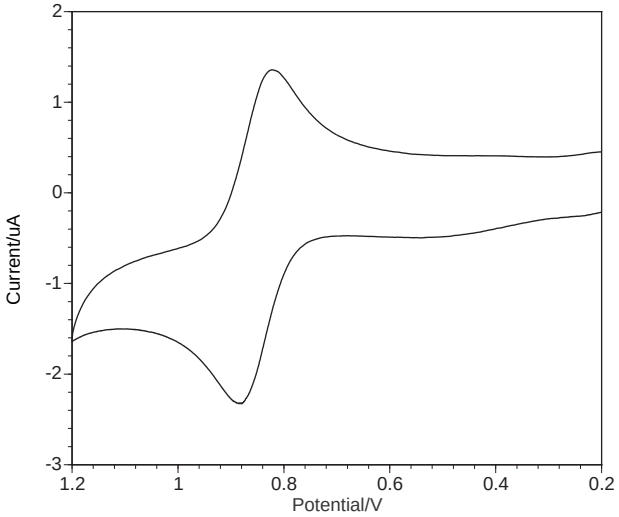

Figure S-4. Oxidation wave of **8a** in acetonitrile containing Et_4NBF_4 (0.1 M) as a supporting electrolyte.

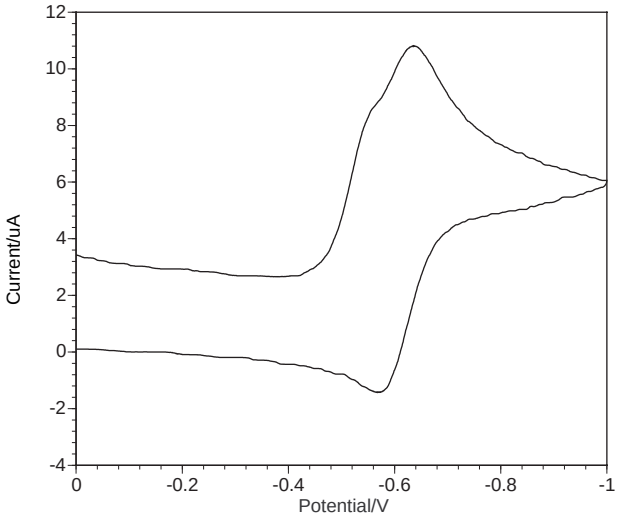

Figure S-5. Reduction wave of **9a** in acetonitrile containing Et_4NBF_4 (0.1 M) as a supporting electrolyte.

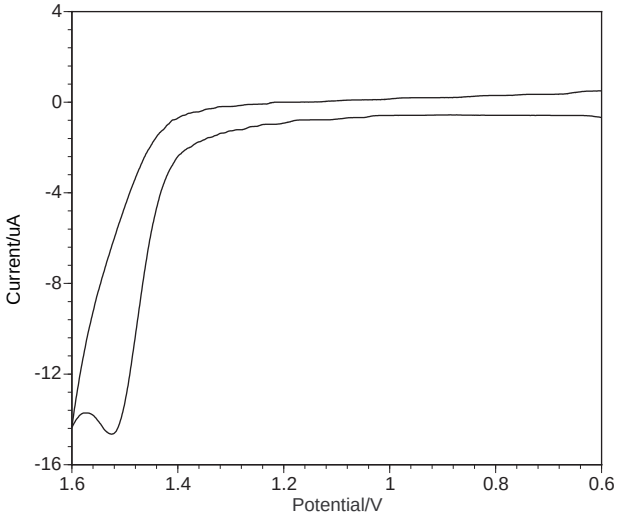

Figure S-6. Oxidation wave of **9a** in acetonitrile containing Et_4NBF_4 (0.1 M) as a supporting electrolyte.

ORTEP drawings and details of the X-ray analysis of compounds 2b and 9b

X-ray crystallographic data for 2b.

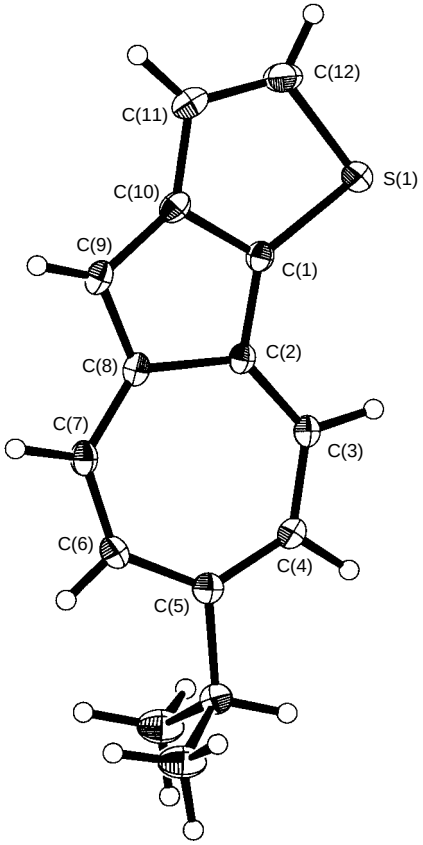

Figure S-7. ORTEP drawing of the molecule **2b** in the crystalline state along with the numbering scheme. Thermal ellipsoids are drawn at the 30% probability level. Selected bond lengths (Å): S(1)–C(1) = 1.727(2), S(1)–C(12) = 1.741(2), C(1)–C(2) = 1.415(2), C(1)–C(10) = 1.401(2), C(2)–C(3) = 1.372(2), C(2)–C(8) = 1.501(2), C(3)–C(4) = 1.409(2), C(4)–C(5) = 1.381(2), C(5)–C(6) = 1.420(2), C(6)–C(7) = 1.377(2), C(7)–C(8) = 1.404(2), C(8)–C(9) = 1.383(2), C(9)–C(10) = 1.426(2), C(10)–C(11) = 1.430(2) and C(11)–C(12) = 1.347(3).

Data and diffraction parameters were obtained for a crystal with dimension 0.20 × 0.20 × 0.05 mm using a Rigaku/MSC mercury CCD diffractometer with Mo–Kα radiation (λ = 0.71070 Å) at –100 °C. Crystal system: monoclinic. Space group: $P2_1/c$ (#14). Unit cell dimensions: a = 9.228(4) Å, b = 6.064(2) Å, c = 22.113(9) Å, β = 106.348(5)°, V = 1187.4(8) Å^3, Z = 4. D_{calcd} = 1.266 g cm^{-3}. μ (Mo–Kα) = 2.40 cm^{-1}. F (000) = 480. 2θ range for data collection = 0.0—54.9°. Number of measured reflections = 10892. Independent reflections = 2639 (R_{int} = 0.021). Final R = 0.036, R_w = 0.093 for 1964 observed reflections (All, 2θ<54.93°). Parameters = 201. GOF = 1.04. $\Delta\rho_{max}$ and $\Delta\rho_{min}$ are 0.23 and –0.17 e$^-$ Å^{-3}, respectively. Refinement method: full-matrix least squares using SHELX-97 program (Sheldrick, 1990), Final $R1$ indices [I>2σI] $R1$ = 0.0356, $wR2$ = 0.0873 and R indices (all data) $R1$ = 0.0458, $wR2$ = 0.0928 for refinement of all non-hydrogen atoms anisotropically and hydrogen atoms isotropically.

The mean deviation from the least-squares plane of the azuleno[1,2-*b*]thiophene moiety is 0.0095 Å. The total internal angle in the seven-membered ring is 900.0°, which is of that of an idealized seven-membered ring. The largest torsion angle in the seven-membered ring is observed around the C(2)–C(8) bond, but the angle is only –2.0(3)°.

X-ray crystallographic data for 9b.

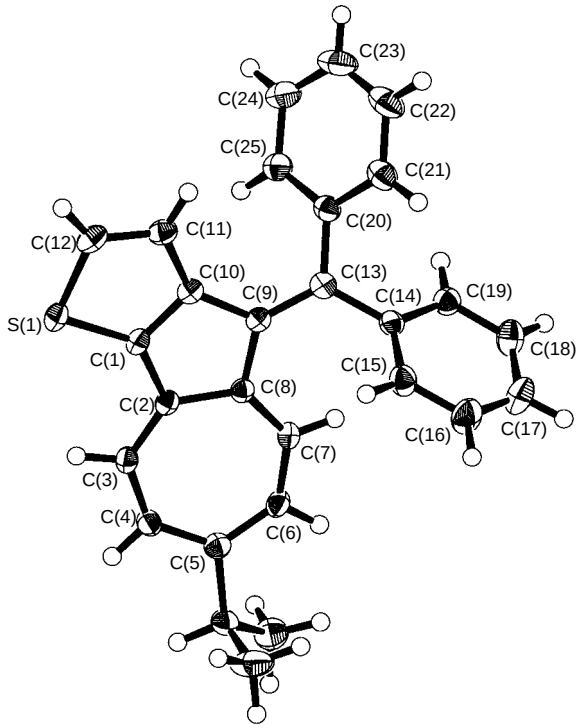

Figure S-8. ORTEP drawing of **9b**·FF_6^-·DDQ in the crystalline state along with the numbering scheme. Thermal ellipsoids are drawn at the 30% probability level. The hexafluorophosphate counter anion and the DDQ molecule incorporated are omitted for clarity.

Data and diffraction parameters were obtained for a crystal with dimension 0.25 × 0.25 × 0.08 mm using a Rigaku/MSC mercury CCD diffractometer with Mo–Kα radiation (λ = 0.71070 Å) at –100 °C. Crystal system: monoclinic. Space group: $P2_1/c$ (#14). Unit cell dimensions: a = 11.160(4) Å, b = 28.552(9) Å, c = 9.773(4) Å, β = 108.615(5)°, V = 2950(1) Å^3, Z = 4. D_{calcd} = 1.773 g cm^{-3}. μ (Mo–Kα) = 4.28 cm^{-1}. F (000) = 1600. 2θ range for data collection = 0.0—55.0°. Number of measured reflections = 21560. Independent reflections = 6353 (R_{int} = 0.032). Final R =

0.041, R_w = 0.092 for 4279 observed reflections (All, 2θ<52.00°). Parameters = 547. GOF = 1.07. $\Delta\rho_{max}$ and $\Delta\rho_{min}$ are 0.20 and –0.36 e^- $Å^{-3}$, respectively. Refinement method: full-matrix least squares using SHELX-97 program (Sheldrick, 1990). Disordered PF_6^- counter anion was divided into two F_6 atoms with the ratio of 0.7 : 0.3 of occupancy by PART instruction and the geometry were restrained by SADI and also SIMU instruction was applied in F atoms. DDQ molecule was disordered by a center of symmetry with the same occupancy and the molecule was restrained in a planer by FLAT instruction. Final *R*1 indices [$I>2\sigma I$] *R*1 = 0.0411, *wR*2 = 0.0816 and R indices (all data) *R*1 = 0.0692, *wR*2 = 0.0916 for refinement of all non-hydrogen atoms anisotropically and hydrogen atoms isotropically.

Faintly twisted boat conformation was found in the seven-membered ring, in which the greatest torsion angle –11.1(3)° was observed through the C(7)–C(8) bond. The average C–C bond length in the seven-membered ring of **9b** was 1.398 Å, which was slightly shorter than that of **2b** (1.409 Å). The long 3b,8a-bond [1.444(3) Å] exhibits the incompletion of the development of the azulenium ion substructure in the seven-membered ring, although the bond is apparently shorter than that of **2b** (1.501(2) Å). As expected, alternating pattern of the bond-lengths was not observed in the two phenyl rings on **9b**, although the phenyl rings exhibited slightly longer 1,2- and 1,6-bonds [C(14)–C(15), C(14)–C(19), C(20)–C(21) and C(20)–C(25)] compared with those of other ring bonds.

The C-α carbon [C(13)] in **9b** has an exactly planar structure with the sum of intermolecular bond angles around the C-α carbon of 360.0°. However, the relatively shorter C(13)–C(9) bond [1.379(3) Å] compared with C(13)–C(14) and C(13)–C(20) bonds [1.476(3) and 1.475(3) Å, respectively] corresponds to the distribution of a substantial amount of the positive charge into the azuleno[1,2-*b*]thiophene ring. The

distribution is reflected by the dihedral angles of each ring from the least-squares plane defined by the trivalent cationic carbon. Each plane of the two phenyl rings twisted by 46.1° and 35.9°, respectively, from the plane defined by the trivalent cationic carbon, whereas a much smaller dihedral angle (24.2°) was observed for that of the azuleno[1,2-*b*]thiophene ring.

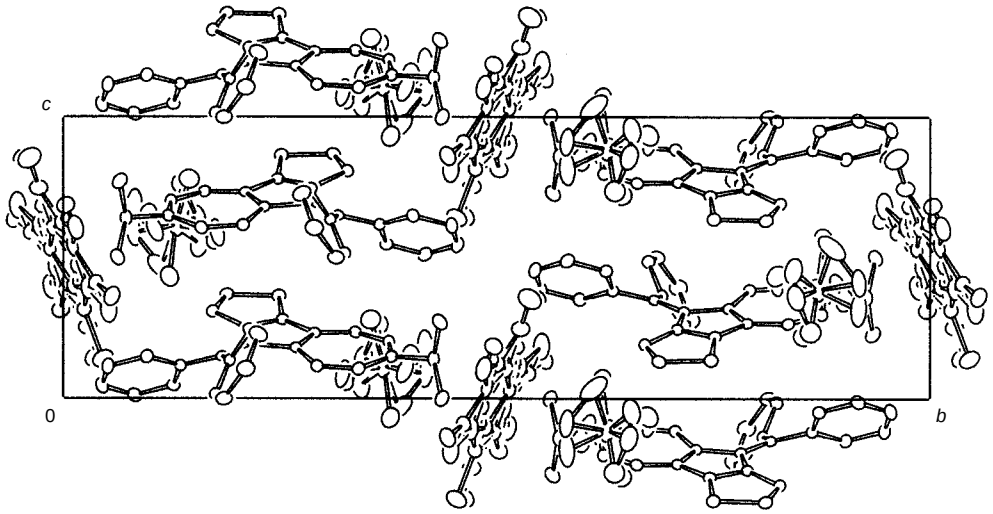

Figure S-9. Projection of the crystal structure of **9b** along *a*-axis.

The crystal structure of **9b**·PF_6^-·DDQ viewed along the *c*-axis is shown in Figure S-9. The counter anion (PF_6^-) was located relatively near the seven-membered ring. There is some interaction between the thiophene ring and the seven-membered part of the neighboring molecule in the single crystal. Closely contacted distances were observed between the overlapping molecules {3.413(3) Å [C(6) and C(11)], 3.473(2) Å [C(7) and C(10)] and 3.485(2) Å [C(7) and C(11)]}. The interatomic distances suggest the π···π intermolecular interactions of the neighboring molecule in the single crystal.

NMR details of compounds reported

Methyl 1,2-Dihydro-6-isopropyl-9-(azuleno[1,2-*b*]thiophene)carboxylate 12.

δ_H (500 MHz, Acetone-d_6) 9.14 (d, *J* 10.2, 1H, 8-H), 7.83 (d, *J* 10.4, 1H, 4-H), 7.34 (d, *J* 10.2, 1.5, 1H, 7-H), 7.26 (d, *J* 10.4, 1.5, 1H, 5-H), 3.87 (t, *J* 7.6, 2H, 1-H), 3.87 (s, 3H, 9-COOMe), 3.61 (t, *J* 7.6, 2H, 2-H), 3.08 (sept, *J* 6.9, 1H, 6-*i*Pr) and 1.33 (d, *J* 6.9, 6H, 6-*i*Pr); δ_C (125 MHz, Acetone-d_6) 165.5 (s, 9-COOMe), 161.4 (C-6), 159.9 (C-9a), 144.9 (C-8a), 135.9 (C-8), 135.8 (C-4), 131.5 (C-3a), 131.3 (C-3b), 126.5 (C-7), 126.0 (C-5), 110.8 (C-9), 51.1 (q, 9-COOMe), 40.2 (d, 6-*i*Pr), 39.7 (C-1), 33.4 (C-2) and 24.3 (q, 6-*i*Pr).

Methyl 1,3-Dihydro-6-isopropyl-9-(azuleno[1,2-*c*]thiophene)carboxylate 13.

δ_H (500 MHz, $CDCl_3$) 9.44 (d, *J* 10.4, 1H, 8-H), 8.07 (d, *J* 10.1, 1H, 4-H), 7.46 (dd, *J* 10.4, 1.5, 1H, 7-H), 7.37 (dd, *J* 10.1, 1.5, 1H, 5-H), 4.60 (t, *J* 2.0, 2H, 1-H), 4.37 (t, *J* 2.0, 2H, 3-H), 3.93 (s, 3H, 9-COOMe), 3.13 (sept, *J* 6.9, 1H, 6-*i*Pr) and 1.37 (d, *J* 6.9, 6H, 6-*i*Pr); δ_C (125 MHz, $CDCl_3$) 165.6 (s, 9-COOMe), 160.9 (C-6), 157.8 (C-9a), 144.4 (C-8a), 137.2 (C-8), 134.6 (C-4), 134.0 (C-3b), 132.5 (C-3a), 127.4 (C-7), 126.2 (C-5), 109.0 (C-9), 51.0 (q, 9-COOMe), 39.7 (d, 6-*i*Pr), 35.7 (C-1), 30.7 (C-3) and 24.3 (q, 6-*i*Pr).

Methyl 6-Isopropyl-9-(azuleno[1,2-*b*]thiophene)carboxylate 14.

δ_H (500 MHz, $CDCl_3$) 9.67 (d, *J* 11.0, 1H, 8-H), 8.48 (d, *J* 9.8, 1H, 4-H), 7.77 (d, *J* 5.0, 1H, 2-H), 7.76 (d, *J* 5.0, 1H, 1-H), 7.53 (dd, *J* 11.0, 1.6, 1H, 7-H), 7.44 (dd, *J* 9.8, 1.6, 1H, 5-H), 4.02 (s, 3H, 9-COOMe), 3.17 (sept, *J* 6.9, 1H, 6-*i*Pr) and 1.39 (d, *J* 6.9, 6H, 6-*i*Pr); δ_C (125 MHz, $CDCl_3$) 165.9 (s, 9-COOMe), 160.2 (C-6), 152.4 (C-9a),

144.4 (C-8a), 137.2 (C-8), 134.3 (C-3b), 133.6 (C-2), 133.0 (C-4), 130.3 (C-3a), 128.1 (C-7), 125.5 (C-5), 121.2 (C-1), 107.6 (C-9), 51.0 (q, 9-COOMe), 39.7 (d, 6-*i*Pr) and 24.3 (q, 6-*i*Pr).

6-Isopropylazuleno[1,2-*b*]thiophene 2b.

δ_H (500 MHz, Acetone-d_6) 8.36 (dd, *J* 9.3, 0.9, 1H, 4-H), 8.31 (d, *J* 10.8, 1H, 8-H), 7.87 (d, *J* 5.0, 1H, 2-H), 7.45 (d, *J* 5.0, 1H, 1-H), 7.43 (br s, 1H, 9-H), 7.20 (dd, *J* 9.3, 1.5, 1H, 5-H), 7.13 (dd, *J* 10.8, 1.5, 1H, 7-H), 3.09 (sept, *J* 6.9, 1H, 6-*i*Pr) and 1.34 (d, *J* 6.9, 6H, 6-*i*Pr); δ_C (125 MHz, Acetone-d_6) 158.6 (C-6), 153.1 (C-9a), 142.4 (C-8a), 137.3 (C-8), 133.5 (C-2), 132.2 (C-3b), 131.6 (C-4), 130.7 (C-3a), 123.1 (C-7), 121.7 (C-5), 119.8 (C-1), 110.0 (C-9), 40.3 (d, 6-*i*Pr) and 24.4 (q, 6-*i*Pr).

9-(Azuleno[1,2-*b*]thiophene)carbaldehyde 15a.

δ_H (400 MHz, $CDCl_3$) 10.61 (s, 1H, 9-CHO), 9.28 (d, *J* 10.3, 1H, 8-H), 8.52 (d, *J* 9.3, 1H, 4-H), 7.89 (d, *J* 5.0, 1H, 2-H), 7.87 (d, *J* 5.0, 1H, 1-H), 7.81 (dd, *J* 9.8, 9.8, 1H, 6-H), 7.59 (dd, *J* 10.3, 9.8, 1H, 7-H) and 7.54 (dd, *J* 9.8, 9.3, 1H, 5-H); δ_C (100 MHz, $CDCl_3$) 183.3 (9-CHO), 153.0 (C-9a), 146.5 (C-8a), 138.1 (C-6), 136.3 (C-2), 136.2 (C-3b), 135.1 (C-8), 133.9 (C-4), 132.3 (C-3a), 129.2 (C-7), 128.5 (C-5), 119.5 (C-1) and 117.3 (C-9).

6-Isopropyl-9-(azuleno[1,2-*b*]thiophene)carbaldehyde 15b.

δ_H (500 MHz, $CDCl_3$) 10.59 (s, 1H, 9-CHO), 9.29 (d, *J* 10.7, 1H, 8-H), 8.52 (d, *J* 9.8, 1H, 4-H), 7.87 (d, *J* 5.0, 1H, 1-H), 7.85 (d, *J* 5.0, 1H, 2-H), 7.59 (dd, *J* 10.7, 1.5, 1H, 7-H), 7.53 (dd, *J* 9.8, 1.5, 1H, 5-H), 3.19 (sept, *J* 6.9, 1H, 6-*i*Pr) and 1.41 (d, *J* 6.9, 6H, 6-*i*Pr); δ_C (125 MHz, $CDCl_3$) 183.0 (9-CHO), 161.3 (C-6), 152.3 (C-9a), 145.7 (C-8a), 135.5 (C-2), 135.2 (C-3b), 135.1 (C-8), 134.0 (C-4), 132.3 (C-3a), 129.4 (C-7),

127.5 (C-5), 119.5 (C-1), 117.0 (C-9), 39.8 (d, 6-*i*Pr) and 24.3 (q, 6-*i*Pr).

Tris[9-(azuleno[1,2-*b*]thienyl)]methane 16a.

δ_H (400 MHz, 50% $CDCl_3/CS_2$) 8.31 (d, *J* 8.8, 3H, 4-H), 8.18 (d, *J* 10.5, 3H, 8-H), 7.69 (s, 1H, CH), 7.40 (dd, *J* 10.5, 9.1, 3H, 6-H), 7.22 (d, *J* 5.1, 3H, 2-H), 7.10 (dd, *J* 10.5, 8.8, 3H, 5-H), 6.83 (dd, *J* 10.5, 9.1, 3H, 7-H) and 5.50 (d, *J* 5.1, 3H, 1-H); δ_C (100 MHz, 50% $CDCl_3/CS_2$) 153.1 (C-9a), 136.7 (C-8a), 135.5 (C-6), 133.5 (C-8), 133.0 (C-3b), 132.6 (C-2), 130.3 (C-4), 129.5 (C-3a), 123.6 (C-9), 122.8 (C-5), 121.4 (C-7), 119.4 (C-1) and 35.8 (CH).

Tris[6-isopropyl-9-(azuleno[1,2-*b*]thienyl)]methane 16b.

δ_H (500 MHz, 50% $CDCl_3/CS_2$) 8.17 (d, *J* 9.5, 3H, 4-H), 8.06 (d, *J* 11.0, 3H, 8-H), 7.55 (s, 1H, CH), 7.14 (d, *J* 5.1, 3H, 2-H), 6.97 (dd, *J* 9.5, 1.5, 3H, 5-H), 6.72 (dd, *J* 11.0, 1.5, 3H, 7-H), 5.52 (d, *J* 5.1, 3H, 1-H), 2.93 (sept, *J* 6.8, 3H, 6-*i*Pr), 1.29 (d, *J* 6.8, 9H, 6-*i*Pr) and 1.28 (d, *J* 6.8, 9H, 6-*i*Pr); δ_C (125 MHz, 50% $CDCl_3/CS_2$) 156.6 (C-6), 152.2 (C-9a), 135.5 (C-8a), 133.1 (C-8), 131.5 (C-2 and C-3b), 130.0 (C-4), 129.3 (C-3a), 123.5 (C-9), 121.4 (C-7), 120.5 (C-5), 119.5 (C-1), 39.6 (d, 6-*i*Pr), 35.4 (CH) and 24.1 (q, 6-*i*Pr).

Bis[9-(azuleno[1,2-*b*]thienyl)]phenylmethane 18a.

δ_H (400 MHz, 50% $CDCl_3/CS_2$) 8.29 (d, *J* 8.8, 2H, 4-H), 8.19 (d, *J* 10.5, 2H, 8-H), 7.41 (dd, *J* 10.5, 9.3, 2H, 6-H), 7.36 (d, *J* 5.1, 2H, 2-H), 7.25—7.23 (m, 3H, 3',4',5'-H), 7.17—7.15 (m, 2H, 2',6'-H), 7.09 (dd, *J* 10.5, 8.8, 2H, 5-H), 7.02 (s, 1H, CH), 6.89 (dd, *J* 10.5, 9.3, 2H, 7-H) and 5.94 (d, *J* 5.1, 2H, 1-H); δ_C (100 MHz, 50% $CDCl_3/CS_2$) 153.1 (C-9a), 144.0 (C-1'), 136.9 (C-8a), 135.5 (C-6), 133.4 (C-8), 133.1 (C-3b), 132.4 (C-2), 130.3 (C-4), 129.7 (C-3a), 129.2 (C-2',6'), 128.3 (C-3',5'), 126.5

(C-4'), 123.6 (C-9), 122.9 (C-5), 121.5 (C-7), 119.6 (C-1) and 42.3 (CH).

Bis[6-isopropyl-9-(azuleno[1,2-*b*]thienyl)]phenylmethane 18b.

δ_H (500 MHz, $CDCl_3$) 8.25 (d, *J* 9.3, 2H, 4-H), 8.18 (d, *J* 11.1, 2H, 8-H), 7.34 (d, *J* 5.1, 2H, 2-H), 7.25—7.24 (m, 3H, 3',4',5'-H), 7.18—7.16 (m, 2H, 2',6'-H), 7.03 (dd, *J* 9.3, 1.5, 2H, 5-H), 7.01 (s, 1H, CH), 6.87 (dd, *J* 11.1, 1.5, 2H, 7-H), 6.01 (d, *J* 5.1, 2H, 1-H), 2.98 (sept, *J* 6.9, 2H, 6-*i*Pr) and 1.30 (d, *J* 6.9, 12H, 6-*i*Pr); δ_C (125 MHz, $CDCl_3$) 157.3 (C-6), 152.4 (C-9a), 144.5 (C-1'), 135.9 (C-8a), 133.1 (C-8), 131.7 (C-3b), 131.4 (C-2), 130.2 (C-4), 129.6 (C-3a), 129.2 (C-2',6'), 128.3 (C-3',5'), 126.4 (C-4'), 123.5 (C-9), 121.9 (C-7), 120.7 (C-5), 119.6 (C-1), 42.1 (CH), 39.6 (d, 6-*i*Pr), 24.2 (q, 6-*i*Pr) and 24.1 (q, 6-*i*Pr).

[9-(Azuleno[1,2-*b*]thienyl)]diphenylmethane 20a.

δ_H (400 MHz, $CDCl_3$) 8.30 (d, *J* 8.8, 1H, 4-H), 8.25 (d, *J* 10.5, 1H, 8-H), 7.48 (d, *J* 5.1, 1H, 2-H), 7.42 (dd, *J* 10.6, 9.2, 1H, 6-H), 7.28—7.16 (m, 10H, 2',3',4',5',6'-H), 7.09 (dd, *J* 10.6, 8.8, 1H, 5-H), 6.96 (dd, *J* 10.5, 9.2, 1H, 7-H), 6.37 (d, *J* 5.1, 1H, 1-H) and 6.31 (s, 1H, CH); δ_C (100 MHz, $CDCl_3$) 153.0 (C-9a), 143.9 (C-1'), 137.0 (C-8a), 135.7 (C-6), 133.4 (C-8), 133.1 (C-3b), 132.4 (C-2), 130.3 (C-4), 129.9 (C-3a), 129.2 (C-2',6'), 128.3 (C-3',5'), 126.3 (C-4'), 124.0 (C-9), 122.9 (C-5), 121.6 (C-7), 119.6 (C-1) and 49.2 (CH).

[6-Isopropyl-9-(azuleno[1,2-*b*]thienyl)]diphenylmethane 20b.

δ_H (600 MHz, $CDCl_3$) 8.24 (d, *J* 9.3, 1H, 4-H), 8.21 (d, *J* 11.1, 1H, 8-H), 7.44 (d, *J* 5.1, 1H, 2-H), 7.26 (m, 4H, 3',5'-H), 7.21 (m, 2H, 4'-H), 7.18 (m, 4H, 2',6'-H), 7.04 (dd, *J* 9.3, 1.6, 1H, 5-H), 6.95 (dd, *J* 11.1, 1.6, 1H, 7-H), 6.36 (d, *J* 5.1, 1H, 1-H), 6.29 (s, 1H, CH), 3.00 (sept, *J* 6.8, 1H, 6-*i*Pr) and 1.32 (d, *J* 6.8, 6H, 6-*i*Pr); δ_C (150

MHz, $CDCl_3$) 157.5 (C-6), 152.1 (C-9a), 144.0 (C-1'), 136.0 (C-8a), 133.0 (C-8), 131.7 (C-3b), 131.4 (C-2), 130.3 (C-4), 129.9 (C-3a), 129.3 (C-2',6'), 128.3 (C-3',5'), 126.3 (C-4'), 123.7 (C-9), 121.9 (C-7), 120.8 (C-5), 119.6 (C-1), 49.1 (CH), 39.6 (d, 6-*i*Pr) and 24.2 (q, 6-*i*Pr).

Tris[9-(azuleno[1,2-*b*]thienyl)]methylium Hexafluorophosphate (7a·PF_6^-).

δ_H (600 MHz, $(CDCl_2)_2$) δ = 8.71—8.67 (m, 3H, ***A***-4-H and 3H, ***B***-4-H), 8.12 (d, *J* 10.3, 3H, ***A***-8-H), 7.92 (d, 1H, ***B***-8-H), 7.91 (d, 1H, ***B***-8-H), 7.84 (dd, 3H, ***A***-6-H), 7.80 (dd, 1H, ***B***-6-H), 7.78 (dd, 3H, ***A***-5-H), 7.78 (dd, 1H, ***B***-6-H), 7.75 (dd, 1H, ***B***-5-H), 7.73 (dd, 1H, ***B***-5-H and 1H, ***B***-6-H), 7.70 (dd, 1H, ***B***-5-H and d, 1H, ***B***-8-H), 7.64 (d, *J* 5.1, 1H, ***B***-2-H), 7.58 (d, *J* 5.1, 1H, ***B***-2-H), 7.56 (d, *J* 5.1, 1H, ***B***-2-H), 7.50 (d, *J* 5.1, 3H, ***A***-2-H), 7.25 (dd, *J* 10.3, 9.5, 3H, ***A***-7-H), 7.18 (dd, 1H, ***B***-7-H), 7.11 (dd, 1H, ***B***-7-H), 7.05 (dd, 1H, ***B***-7-H), 6.29 (d, *J* 5.1, 1H, ***B***-1-H), 6.09 (d, *J* 5.1, 1H, ***B***-1-H), 6.05 (d, *J* 5.1, 1H, ***B***-1-H) and 5.87 (d, *J* 5.1, 3H, ***A***-1-H); δ_C (125 MHz, $(CDCl_2)_2$) 155.2 (***A***-C-9a and ***B***-C-9a), 155.0 (2C, ***B***-C-9a), 150.5 (***B***-C-8a), 150.4 (***B***-C-8a), 149.3 (***A***-C-8a and ***B***-C-8a), 148.3 (C^+), 148.1 (C^+), 142.1 (***B***-C-3b), 141.9 (***A***-C-3b), 141.6 (***B***-C-3b and ***B***-C-6), 141.5 (***B***-C-3b), 141.2 (***A***-C-6 and ***B***-C-6), 140.8 (***B***-C-6), 138.9 (***A***-C-8), 138.5 (***B***-C-8), 138.3 (***B***-C-2 and ***B***-C-8), 138.0 (***B***-C-8), 137.8 (***A***-C-2 and 2C, ***B***-C-2), 136.8 (***B***-C-3a), 136.3 (***A***-C-3a and ***B***-C-3a), 136.2 (C-4), 135.9 (C-4), 135.8 (C-4 and ***B***-C-3a), 135.6 (C-4), 133.1 (***B***-C-5), 133.0 (***B***-C-7), 132.9 (***A***-C-5 and ***A***-C-7), 132.6 (***B***-C-5 and ***B***-C-7), 132.5 (***B***-C-5 and ***B***-C-7), 123.6 (C-9), 123.3 (C-9), 121.0 (***B***-C-1), 120.7 (***B***-C-1), 120.6 (***B***-C-1) and 120.3 (***A***-C-1).

Tris[6-isopropyl-9-(azuleno[1,2-*b*]thienyl)]methylium Hexafluorophosphate (7b·PF_6^-).

δ_H (600 MHz, C_6D_6:$CDCl_3$ = 1:30) 8.71 (d, *J* 10.0, 1H, ***B***-4-H), 8.64 (d, *J* 9.9,

1H, ***B***-4-H), 8.63 (d, *J* 9.9, 3H, ***A***-4-H), 8.62 (d, 1H, ***B***-4-H), 8.15 (d, *J* 10.6, 3H, ***A***-8-H), 7.95 (d, *J* 10.8, 1H, ***B***-8-H), 7.91 (d, *J* 10.7, 1H, ***B***-8-H), 7.75 (d, *J* 10.0, 1H, ***B***-5-H), 7.72 (d, *J* 10.6, 1H, ***B***-8-H), 7.70 (d, *J* 9.9, 3H, ***A***-5-H), 7.65 (d, 1H, *J* 9.9, ***B***-5-H and 1H, ***B***-5-H), 7.54 (d, *J* 5.0, 1H, ***B***-2-H), 7.49 (d, *J* 5.0, 1H, ***B***-2-H), 7.47 (d, *J* 5.0, 1H, ***B***-2-H), 7.39 (d, *J* 5.1, 3H, ***A***-2-H), 7.20 (d, *J* 10.6, 3H, ***A***-7-H), 7.12 (d, *J* 10.8, 1H, ***B***-7-H), 7.05 (d, *J* 10.7, 1H, ***B***-7-H), 6.98 (d, *J* 10.6, 1H, ***B***-7-H), 6.28 (d, *J* 5.0, 1H, ***B***-1-H), 6.14 (d, *J* 5.0, 1H, ***B***-1-H), 6.08 (d, *J* 5.0, 1H, ***B***-1-H), 5.95 (d, *J* 5.1, 3H, ***A***-H1), 3.09—2.98 (m, 3H, ***A***-6-*i*Pr and 3H, ***B***-6-*i*Pr) and 1.29—1.19 (m, 18H, ***A***-6-*i*Pr and 18H, ***B***-6-*i*Pr); δ_C (125 MHz, $CDCl_3$) 165.1 (C-6), 164.5 (2C, C-6), 163.9 (C-6), 154.2 (***B***-C-9a), 154.1 (***A***-C-9a), 153.9 (2C, ***B***-C-9a), 148.9 (***B***-C-8a), 148.7 (***B***-C-8a), 147.9 (C^+), 147.7 (***A***-C-8a), 147.5 (C^+), 147.4 (***B***-C-8a), 140.7 (***B***-C-3b), 140.1 (***A***-C-3b), 140.0 (***B***-C-3b), 139.5 (***B***-C-3b), 138.6 (***A***-C-8), 138.1 (***B***-C-8), 137.8 (***B***-C-8), 137.6 (***B***-C-8), 136.6 (***B***-C-2), 136.5 (***B***-C-3a), 136.3 (***B***-C-2), 136.0 (***A***-C-2 and ***B***-C-4), 135.9 (***B***-C-2), 135.7 (***B***-C-3a), 135.6 (***A***-C-3a), 135.5 (***B***-C-4), 135.3 (***A***-C-4), 135.0 (***B***-C-3a), 134.9 (***B***-C-4), 132.0 (***B***-C-5 and ***A***- and *B*-C-7), 131.5 (2C, ***B***-C-7), 131.4 (***A***-C-5), 131.2 (***B***-C-5), 130.7 (***B***-C-5), 123.3 (C-9), 122.9 (C-9), 120.5 (***B***-C-1), 120.3 (***B***-C-1), 120.2 (***B***-C-1), 120.0 (***A***-C-1), 39.7 (d, 6-*i*Pr), 39.7 (d, 6-*i*Pr), 39.7 (d, 6-*i*Pr), 24.2 (q, 6-*i*Pr), 24.0 (q, 6-*i*Pr), 23.9 (q, 6-*i*Pr) and 23.9 (q, 6-*i*Pr).

Bis[9-(azuleno[1,2-*b*]thienyl)]phenylmethylium Hexafluorophosphate (8a·PF_6^-).

δ_H (500 MHz, $(CDCl_2)_2$, 50 °C) 8.72—8.70 (m, 2H, 4-H), 7.99—7.92 (m, 4H, 5,6-H), 7.93 (d, *J* 10.1, 2H, 8-H), 7.75 (tt, *J* 7.5, 1.2, 1H, 4'-H), 7.71 (d, *J* 5.1, 2H, 2-H), 7.53 (dd, *J* 8.3, 7.5, 2H, 3',5'-H), 7.45 (dd, *J* 8.3, 1.2, 2H, 2',6'-H), 7.44—7.39 (m, 2H, 7-H) and 6.12 (d, *J* 5.1, 2H, 1-H); δ_C (125 MHz, $(CDCl_2)_2$, 50 °C) 158.3 (C^+), 155.9 (C-9a), 152.2 (C-8a), 145.0 (C-3b), 142.5 (C-6), 141.4 (C-1'), 140.1 (C-8), 139.2 (C-2), 138.4 (C-3a), 136.6 (C-4), 136.1 (C-5), 135.5 (C-7), 133.6 (C-2',6'), 133.5 (C-4'),

130.0 (C-3',5'), 125.2 (C-9) and 121.4 (C-1).

Bis[6-isopropyl-9-(azuleno[1,2-*b*]thienyl)]phenylmethylium Hexafluorophosphate (8b·PF_6^-).

δ_H (500 MHz, CD_2Cl_2) 8.69 (d, *J* 10.3, 2H, 4-H), 7.91 (d, *J* 10.7, 2H, 8-H), 7.89 (dd, *J* 10.3, 1.8, 2H, 5-H), 7.76 (tt, *J* 7.5, 1.3, 1H, 4'-H), 7.67 (d, *J* 5.0, 2H, 2-H), 7.56 (dd, *J* 8.2, 7.5, 2H, 3',5'-H), 7.47 (dd, *J* 8.2, 1.3, 2H, 2',6'-H), 7.31 (dd, *J* 10.7, 1.8, 2H, 7-H), 6.16 (d, *J* 5.0, 2H, 1-H), 3.12 (sept, *J* 6.9, 2H, 6-*i*Pr) and 1.29 (d, *J* 6.9, 12H, 6-*i*Pr); δ_C (125 MHz, CD_2Cl_2) 166.8 (C-6), 157.8 (C^+), 155.3 (C-9a), 150.9 (C-8a), 143.7 (C-3b), 141.9 (C-1'), 140.0 (C-8), 138.3 (C-3a), 137.7 (C-2), 136.4 (C-4), 135.2 (C-5), 134.6 (C-7), 133.7 (C-2',6'), 133.2 (C-4'), 129.9 (C-3',5'), 125.3 (C-9), 121.6 (C-1), 40.3 (d, 6-*i*Pr), 24.1 (q, 6-*i*Pr) and 24.1 (q, 6-*i*Pr).

[9-(Azuleno[1,2-*b*]thienyl)]diphenylmethylium Hexafluorophosphate (9a·PF_6^-).

δ_H (500 MHz, $CDCl_3$) 8.70 (d, *J* 9.9, 1H, 4-H), 8.34 (dd, *J* 9.9, 9.5, 1H, 5-H), 8.22 (dd, *J* 9.8, 9.5, 1H, 6-H), 8.03 (d, *J* 9.8, 1H, 8-H), 7.88 (dd, *J* 9.8, 9.8, 1H, 7-H), 7.83 (d, *J* 5.1, 1H, 2-H), 7.70 (tt, *J* 7.4, 1.2, 1H, 4''-H), 7.69 (tt, *J* 7.5, 1.2, 1H, 4'-H), 7.53 (dd, *J* 8.2, 7.5, 2H, 3',5'-H), 7.50 (dd, *J* 8.2, 7.4, 2H, 3'',5''-H), 7.40 (dd, *J* 8.2, 1.2, 1H, 2',6'-H), 7.24 (dd, *J* 8.2, 1.2, 2H, 2'',6''-H) and 6.37 (d, *J* 5.1, 1H, 1-H); δ_C (125 MHz, $CDCl_3$) 168.5 (C^+), 158.5 (C-8a), 157.2 (C-9a), 154.1 (C-3b), 146.0 (C-6), 144.8 (C-5), 143.9 (C-8), 143.6 (C-3a), 142.6 (C-2), 141.9 (C-7), 140.6 (C-1' or C-1''), 139.8 (C-1' or C-1''), 138.5 (C-4), 134.4 (C-4''), 134.3 (C-2'',6''), 134.1 (C-4'), 133.4 (C-2',6'), 130.5 (C-9), 129.9 (C-3'',5''), 129.8 (C-3',5') and 123.1 (C-1).

[6-Isopropyl-9-(azuleno[1,2-*b*]thienyl)]diphenylmethylium Hexafluorophosphate (9b·PF_6^-).

δ_H (600 MHz, $CDCl_3$) 8.80 (d, *J* 10.6, 1H, 4-H), 8.45 (dd, *J* 10.6, 1.8, 1H, 5-H), 8.08 (d, *J* 10.4, 1H, 8-H), 7.86 (dd, *J* 10.4, 1.8, 1H, 7-H), 7.76 (d, *J* 5.0, 1H, 2-H), 7.73 (tt, *J* 7.5, 1.2, 1H, 4'-H or 4"-H), 7.70 (tt, *J* 7.5, 1.2, 1H, 4'-H or 4"-H), 7.57 (dd, *J* 8.3, 7.5, 2H, 3',5'-H or 3",5"-H), 7.57 (dd, *J* 8.3, 7.5, 2H, 3',5'-H or 3",5"-H), 7.45 (dd, *J* 8.3, 1.2, 2H, 2',6'-H or 2",6"-H), 7.33 (dd, *J* 8.3, 1.2, 2H, 2',6'-H or 2",6"-H), 6.36 (d, *J* 5.0, 1H, 1-H), 3.29 (sept, *J* 6.8, 1H, 6-*i*Pr) and 1.39 (d, *J* 6.8, 1H, 6-*i*Pr); δ_C (150 MHz, $CDCl_3$) 171.5 (C-6), 165.8 (C^+), 156.2 (C-8a), 155.5 (C-9a), 153.2 (C-3b), 145.4 (C-5), 143.6 (C-3a), 143.5 (C-8), 140.9 (C-1' or C-1"), 140.7 (C-7), 140.4 (C-2), 139.7 (C-1' or C-1"), 138.4 (C-4), 133.5 (C-2',6' or C-2",6"), 133.4 (C-4' or C-4"), 132.8 (C-4' or C-4"), 132.6 (C-2',6' or C-2",6"), 130.7 (C-9), 129.5 (C-3',5' or C-3",5"), 129.3 (C-3',5' or C-3",5"), 122.7 (C-1), 40.1 (d, 6-*i*Pr) and 23.7 (q, 6-*i*Pr).