Supporting information

Azulene Containing Organic Chromophores with Tunable Near IR Absorption in the Range of 0.6 to 1.7 μm

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Experimental details

Materials and Reagents: TFA (Merck, >99%), zinc chloride (Aldrich), and tri-n-butyltin chloride (Fluka) were used without further purification. Chloroform was distilled from calcium hydride and degassed with argon prior to use.

Instrumentation: ¹H-NMR (300 MHz) and ¹³C-NMR (75.5 MHz) data were recorded on a Bruker DPX 300 FT-NMR spectrophotometer. CDCl₃ was the solvent used and chemical shift was expressed relative to Me₄Si as an internal standard. EIMS spectra were obtained using a Micromass 7034E mass spectrometer with relative intensity given in parentheses. TOF mass spectra were acquired on a Bruker ULTRAFLEX TOF mass spectrometer equipped with a nitrogen laser with an emission wavelength of 337 nm. Spectra were obtained in the linear positive mode at an accelerating voltage of 25 kV. Elemental analyses were conducted at the Chemical, Molecular and Materials Analysis Center, Department of Chemistry, National University of Singapore, on a Perkin-Elmer 240C elemental analyzer. The electronic spectra were obtained with a Hewlett Packed 8452A diode array spectrometer or a Perkin-Elmer Lambda 900 UV-vis-NIR spectrometer.
1,3-bis[2-(3-methy-thienyl)]azulene (1): Magnesium (0.9g, 37.5mmol) and 30ml anhydrous ether were placed in a 50ml three-neck round-bottom flask equipped with a magnetic stirrer, condenser and a rubber septum. 3-methyl-2-bromo-thiophene (18mmol) and 1,2-dibromoethane (3.35g, 18mmol) dissolved in 10 ml ether was added dropwise under argon atmosphere in an ice-water bath. After the addition finished, removed the ice-water bath and kept it react at room temperature for 1h and then heated to efflux for another 4h to afford the Grignard reagent. The Grignard reagent was transferred using a cannula into a 100ml three-neck flask containing 1,3-dibromoazulene (1.7g, 6mmol), Ni(dppp)Cl₂ (0.22g) and 30ml anhydrous ether in an ice-water bath. The solution was warmed to reflux for 4h and then left it reacts at room temperature under argon overnight. The reaction was stopped by pouring the mixture into 200 ml dilute HCl solution. The aqueous layer was extracted with ether. The combined organic layers were washed with sodium bicarbonate solution, water and brine successively, dried over magnesium sulphate. Filtered and evaporated off the solvent, the residue was applied to the column (silica gel) with hexane as eluant. \( R_f = 0.58 \) (Hexane). \(^1\)H NMR (CDCl₃, 300 MHz): \( \delta 8.38 \) (d, \( J = 9.7 \)Hz, 2H), 7.97 (s, 1H), 7.63 (t, \( J = 9.7 \)Hz, 1H), 7.33 (d, \( J = 5.2 \)Hz, 2H), 7.19 (d, \( J = 9.7 \)Hz, 2H), 7.06 (d, \( J = 5.2 \)Hz, 2H), 2.24 (s, 6H). \(^{13}\)C NMR (CDCl₃, 75.5MHz): \( \delta 139.9, 138.8, 138.0, 136.6, 134.8, 132.3, 130.4, 124.2, 123.7, 122.0, 15.0 \). MS (EI) m/z (relative intensity): 320 (M⁺, 100). HRMS (EI): calcd for C₂₀H₁₆S₂(M⁺), 320.0693; found, 320.0693. Anal. Calcd for C₂₀H₁₆S₂: C, 74.96; H, 5.03; S, 20.01. Found: C, 74.83; H, 5.10; S, 20.56.

1,3-Bis[2-(5-bromo-3-methyl)thienyl]azulene: To a 100 mL round-bottom flask was added 1,3-bis[2-(3-methyl-thienyl)]azulene (0.96 g, 3 mmol), chloroform (30 mL) and acetic acid (30 mL). The reaction mixture placed in an ice-water bath and NBS (1.06 g, 6 mmol) was added in small portions over 30 min. The reaction mixture was then warmed to room temperature and stirred for 15 h. The reaction was quenched with water (100 mL). The aqueous layer was extracted with chloroform twice. The combined organic layers were then washed successively with sodium bicarbonate solution, water, and brine. The organic layer was dried over MgSO₄ and the product was purified by chromatography on silica gel using hexane as eluant. 1,3-Bis[2-(5-bromo-3-methyl)thienyl]azulene was obtained as a dark green solid (1.22 g, 86%). \(^1\)H-NMR \( \delta 8.56 \) (d, \( J = 9.4 \) Hz, 2H), 7.86 (s, 1H), 7.65 (t, \( J = 9.7 \) Hz, 1H), 7.23 (t, \( J = 9.9 \) Hz, 2H), 7.00 (s, 1H), 2.16 (s, 6H).
13C-NMR δ 140.0, 139.7, 138.6, 137.1, 136.0, 134.2, 133.5, 124.8, 121.3, 110.9, 15.3. MS (EI) m/z 478 (M⁺ + 2, 60), 400 (M⁺-Br, 100).

1,3-Bis(3'-phenyl-thenyl)-azulene (2): Following a similar procedure as compound 1, compound 2 was obtained as green solid, yield 62%. 1H NMR (CDCl₃, 300 MHz): δ 8.20 (d, J = 9.4 Hz, 2H), 7.70 (s, 1H), 7.44 (t, J = 9.4 Hz, 1H), 7.41 (d, J = 5.2, 2H), 7.30 (d, J = 5.2 Hz, 2H), 7.19-7.10 (m, 10H), 6.96 (t, J = 9.9 Hz, 2H). 13C NMR (CDCl₃, 75.5MHz): δ 140.7, 139.3, 138.7, 137.7, 136.7, 136.5, 133.0, 129.5, 128.4, 128.1, 126.5, 124.9, 123.9, 121.8. MS (EI) m/z (relative intensity): 444 (M⁺, 100). HRMS (EI) calculated for C₃₀H₂₀S₂ (M⁺), 444.1006; found, 444.1011.

1,3-Di-(5',5''-phenyl-3',3''-methyl-thienyl)-azulene (3): Into a 50 mL round-bottom flask was placed LiCl (0.38 g), AsPh₃ (97 mg), Pd(PPh₃)₄ (90 mg), compound 1,3-Bis[2-(5-bromo-3-methyl)thienyl]azulene (1.42 g, 3 mmol) and 1,4-dioxane (20 mL). The mixture was stirred under nitrogen atmosphere and phenyl tri-n-butyltin (9 mmol) was added. The reaction mixture was then heated and maintained at 90 °C for 15 h. The mixture was cooled and ethyl acetate (50 mL) was added. The solution was poured into an aqueous KF solution with stirring. Any insoluble materials were filtered off. The organic layer was separated, washed successively with water and brine, and dried over MgSO₄. The product was purified by chromatography on silica gel using 9:1 hexane:ethyl acetate as eluent. Compound 3 was obtained as a dark green solid (0.85g, 61%). 1H-NMR δ 8.49 (d, J = 9.4 Hz, 2H), 8.04 (s, 1H), 7.66 (m, 5H), 7.41 (t, J = 7.8 Hz, 4H), 7.30-7.20 (m, 6H), 2.30 (s, 6H). 13C NMR (CDCl₃, 75.5MHz): δ 142.6, 139.7, 139.1, 138.0, 136.7, 135.8, 134.5, 131.9, 128.8, 127.2, 126.6, 125.5, 123.9, 122.1, 15.3. MS (EI) m/z 472 (M⁺, 100). HRMS (EI) calculated for C₃₂H₂₄S₂ (M⁺), 472.1319; found, 472.1321.

1,3-Di[5'-(5''-phenyl-3''-methyl-thienyl)-3'-methyl-thienyl]-azulene (4): 4 was obtained as green solid following the same procedure as synthesis of compound 3. Weight: 0.9 g, yield: 45%. 1H NMR (CDCl₃, 300 MHz): δ 8.47 (d, J=9.7 Hz, 2H), 8.01 (s, 1H), 7.65 (t, J = 9.7 Hz, 1H), 7.51 (d, J = 7.6 Hz, 4H), 7.43 (t, J = 7.6 Hz, 4H), 7.32 (t, J = 7.6 Hz, 2H), 7.23 (t, J = 9.7 Hz, 2H), 7.14 (s, 2H), 7.05 (s, 2H), 2.34 (s, Me, 6H), 2.24 (s, Me, 6H). 13C NMR (CDCl₃, 75.5MHz): δ 139.6, 139.2, 138.1, 136.7, 136.5, 135.9, 135.6, 135.3, 134.5, 133.9, 131.3, 128.7, 128.5, 127.3, 127.1, 126.9, 124.0, 121.8, 15.2, 15.1. MS (EI) m/z (relative intensity): 664 (M⁺, 100). HRMS (EI) m/z calcd for C₃₂H₂₄S₂, 664.1387; found, 664.1365.
Protonation of compounds 1-4.

The protonation of neutral compound was carried in chloroform solution at atmosphere. To a solution of neutral compound in chloroform, different ratio of TFA was added and the spectra were monitored with a UV-vis-NIR spectrometer. To test the stability of the protonated compounds, the protonated compounds solution (TFA/CHCl₃, v/v, 30/70) was sealed in a cuvette and leave at room temperature. The UV-vis-NIR spectra of the aged protonated compounds were measured by using a UV-vis-NIR spectrometer. To measure the ¹H-NMR spectra of protonated compound, neutral compounds were first dissolved in CDCl₃ and then 30% TFA-D (in volume) was added before NMR measurement. To rule out the possibility that the bathochromic shift come from molecular association, different concentration of the compounds was measured range from $2 \times 10^{-5}$ M to $1 \times 10^{-6}$ M. The results show there is no obvious shift of the spectra, suggests the shift was not due to molecular association.

**Figure S1.** ¹H-NMR and ¹³C-NMR spectra of 1,3-bis[2-(3-methy-thienyl)]azulene (1).
**Figure S2.** $^1$H-NMR and $^{13}$C-NMR spectra of 1,3-Bis[2-(5-bromo-3-methyl)thienyl]azulene.
Figure S3. $^1$H-NMR and $^{13}$C-NMR spectra of 1,3-Di-(5',5''-phenyl-3',3''-methyl-thienyl)-azulene (2).
Figure S4. $^1$H-NMR (a) and 2-D HMQC (b) spectra of compound 3.
Figure S5. H\textsuperscript{1}-NMR (a) and 2-D HMQC (b) spectra of compound 4.
Figure S6. Comparison of UV-vis-IR spectra of protonated compound 3A after 6 month standing at room temperature.