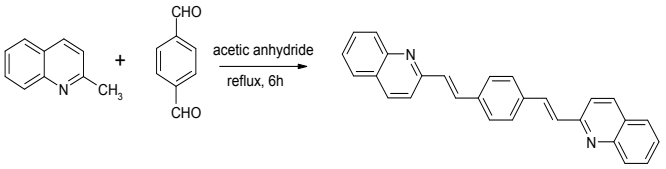
Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supplementary information

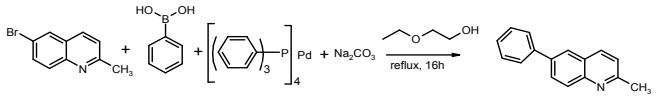
Preparation of 1, 4-[Bis(2,2'-quinolinyl)vinyl)] benzene (E278-ST)



A mixture of quinaldine (46.8 g; 0.35 mole) and tere-phthaldicarboxaldehyde (25.0 g; 0.17 mole) was refluxed in acetic anhydride (70 ml) for 6 hours. The reaction mixture was allowed to cool overnight. Methanol was added to the reaction mixture and the product was filtered off under suction. The filter cake was washed thoroughly with de-ionised water, followed by methanol. The deep yellow crystalline solid was dried under vacuum at 80 °C for 8 hours. Yield: quantitative.The product was sublimed purified. Mp 246 °C (DSC, onset). Elemental analysis: Found C 87.44, H 5.37, N 7.34 %. $C_{28}H_{20}N_2$ requires, C 87.47, H 5.24 and N 7.29 %. Fluorescence (Chloroform): λ_{max}(emission): 439 nm, excitation wavelength: 340 nm. Fluorescence (powder): λ_{max} (emission): 487 nm, excitation wavelength: 380 nm. Fluorescence (Thin film): λ_{max} (emission): 455 and 480 (sh) nm, UV-Vis (Chloroform) λ_{max} (absorption)/nm (ε)/$M^{-1}cm^{-1}$: 298 (14,970) and 379 (49,024). UV-Vis (thin film) λ_{max} (absorption)/nm: 302 and 418 (sh). TGA/°C (weight loss %): 400 (0), Optical band gap: 2.4 eV. Cyclic voltammetry: HOMO -6.0 eV and LUMO -3.6 eV.

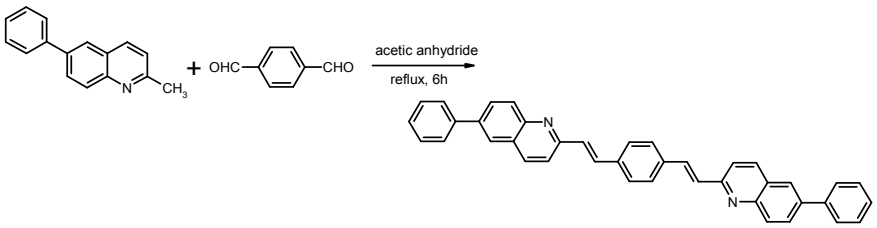
Synthesis of E278-Ph-ST

a) Preparation of 2-Methyl-6-phenylquinoline



2-Methyl-6-phenylquinoline was prepared from 6-bromo-2-methylquinoline by Suzuki coupling with phenylboronic acid and tetrakis(triphenylphosphine) palladium(0) in refluxing 2-ethoxyethanol. To a solution 6-Bromo-2-methylquinoline (8.9g; 40 mmol) in 2-ethoxyethanol (100 ml) was added tetrakis(triphenylphosphine)palladium (1 g; 0.86 mmol) and the reaction mixture was stirred at room temperature for 10 minutes. Phenylboronic acid (5g; 41 mmol) in ethoxyethanol (50 ml) was then added followed by aqueous sodium carbonate (8.4 g; 79 mmol) in water (50 ml). The reaction mixture was magnetically stirred and refluxed for 16 h. The cooled reaction mixture was extracted with chloroform (3 x 100 ml), washed with brine, dried over anhydrous magnesium sulphate and solvent concentrated. The residue with the solvent was filtered through a silica gel column and the colourless solution was evaporated. The residue was triturated with petroleum spirit (30 – 40°C boiling fraction) and recrystallised from diethyl ether to give an off-white solid, 5.5 g (63 %); Mp 95 °C (DSC, onset). Anal: Found, C 87.60, H 5.98, N 6.32 %; $C_{16}H_{13}N$ requires, C 87.64, H 5.98 and N 6.39 %.

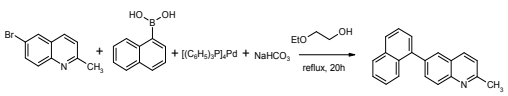
b) Preparation of 1, 4-[Bis(6,6'-phenyl-2,2'quinolin-2-yl)vinyl)] benzene



A mixture of 2-methyl-6-phenylquinoline (5.2 g; 24 mmol) and terephthaldicarboxaldehyde (1.6 g; 12 mmol) in acetic anhydride (20 ml) was refluxed under nitrogen atmosphere for 6 hours. To the cooled reaction mixture methanol (50 ml) and water (10 ml) were added and the shiny yellowish solid was filtered off, washed well with methanol, water and finally with diethyl ether. The product was dried under vacuum at 80 °C. Yield 4.6 g (72 %). Mp 312 °C (DSC, onset). The product was further purified by sublimation. Elemental analysis: Found C 89.46, H 5.25, N 5.22 %. $C_{40}H_{28}N_2$, requires C 89.52, H 5.26 and N 5.22 %. Fluorescence (chloroform): λ_{max} (emission): 429 nm, excitation wavelength: 340 nm. Fluorescence (powder): λ_{max} (emission): 500 and 531 nm, excitation wavelength: 340 nm. Fluorescence (thin film): λ_{max} (emission): 534 nm, UV-Vis (chloroform) λ_{max} (absorption)/nm (ε)/$M^{-1}cm^{-1}$: 255 (99,800) and 393 (10,000) . UV-Vis (thin film) λ_{max} (absorption)/nm: 306, 372 and 442 (sh). TGA/°C (weight loss %): 400 (0), Optical band gap: 2.6 eV

Synthesis of E278-Np-ST

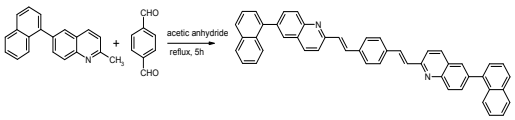
a) Preparation of 6-(1-Naphthyl)-2-methylquinoline



6-Bromo-2-methylquinoline (32.5; 0.145 mole) was dissolved in 2-ethoxyethanol (200 ml) and to the magnetically stirred solution under nitrogen was added tetrakis(triphenylphosphine)palladium (5.1 g; 0.0044 mole) followed by 2-ethoxyethanol (25 ml). After 5 minutes stirring at room temperature 1-naphthaleneboronic acid (25.0 g; 0.145 mole) was added followed by 2-ethoxyethanol (75 ml). Sodium hydrogencarbonate (35 g; 0.42 mole) in water (200 ml) was added all at once and the reaction mixture was stirred and heated under nitrogen atmosphere at 90 °C for 20 h. The reaction mixture became orange in colour. The reaction mixture was allowed to cool, dichloromethane (100 ml) was added and the product was filtered off under suction using celite, with a layer of silica gel on the top. To the filtrate further dichloromethane (250 ml) was added and the resulting solution wasextracted with de-ionised water (2 x 300 ml) and then with brine (250 ml). The organic phase was dried over anhydrous magnesium sulphate and the solvent removed to give a thick liquid. Trituration with diethyl ether and cooling in the refrigerator gave a light yellow solid. The product was dried under vacuum at 80 °C, (22 g; 56 %). Mp 111 °C, (DSC, onset). Anal: Found C 89.16, H 5.58 and N 5.15 %, C_{20} H_{15}N requires, C 89.19, H 5.61 and N 5.20 %.

Comment [AJB]: How?

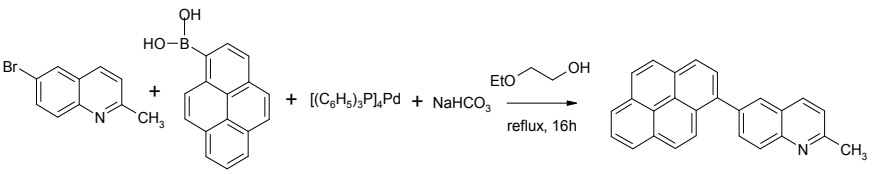
b) Preparation of 1,4-[Bis(6,6'-naphthyl-2,2'quinolin-2-yl)vinyl)]benzene



A mixture of 6-naphthyl-2-methylquinoline (11 g; 0.041 mole) and terephthaldicarboxaldehyde (2.75 g; 0.02 mole) was refluxed in acetic anhydride (30 ml) for 6h. During this time a yellow solid separated out from the reaction mixture. To the cooled reaction mixture methanol (50 ml) was added and the product filtered off under suction. The filter cake was washed with de-ionised water and then with methanol to remove any traces of acetic anhydride. The product was dried under vacuum at 80 °C, yield 9.5 g (73 %). Mp 276 °C (DSC, onset), T_g 94 °C. The product further purified by sublimation. Elemental analysis; Found: C 89.81, H 5.12, N 4.24 %, $C_{48}H_{32}N_2$ requires, C 90.54, H 5.07 and N 4.40 %. Fluorescence (chloroform): λ_{max} (emission): 430 nm, excitation wavelength: 380 nm. Fluorescence (powder): λ_{max} (emission): 495 nm, excitation wavelength: 380 nm. Fluorescence (thin film): λ_{max} (emission): 521 nm, UV-Vis (chloroform) λ_{max} (absorption)/nm (ε)/$M^{-1}cm^{-1}$: 242 (56, 573), 292 (31, 032) and 388 (40, 798) . UV-Vis (thin film) λ_{max} (absorption)/nm: 224, 290 and 364 nm. TGA/°C (weight loss %): 400 (0.5), Optical band gap: 2.8 eV.

Synthesis of E278-PyR-ST

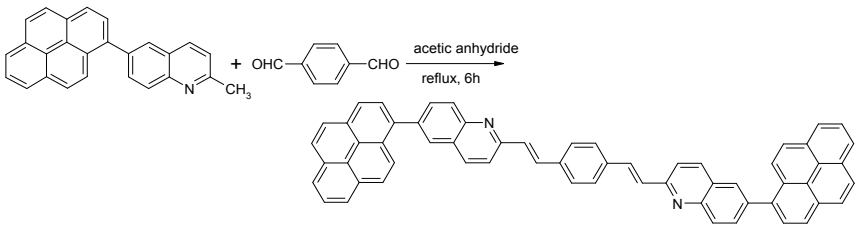
a) Preparation of 6-Pyrenyl-2-methylquinoline



6-Bromo-2-methylquinoline (4.5g; 20mmol) was dissolved in 2-ethoxyethanol (30 ml) and to the magnetically stirred solution under nitrogen was added tetrakis(triphenylphosphine)palladium (1 g; 0.9 mmol). After 5 minutes stirring at room temperature, 1-pyreneboronic acid (5.0 g; 20mmol) was added followed by 2-ethoxyethanol (10 ml). Sodium hydrogencarbonate (10 g; 94 mmol) in water (60 ml) was added all at once and the reaction mixture was stirred and heated under nitrogen atmosphere at 90 °C for 18 h. The reaction mixture was allowed to cool, dichloromethane (100 ml) was added and the reaction mixture was filtered through a layer of silica gel. To the filtrate further dichloromethane (50 ml) was added and extracted with de-ionised water (2 x 100 ml). The organic phase was dried over anhydrous magnesium sulphate and the solvent removed to give the required product. The product was dried under vacuum at 80 °C, Yield 4.5 g (67 %). Mp 133 °C (DSC, onset). Anal: Found: C 90.80, H 5.09 and N 4.32 %. C26H17N requires, C 90.93, H 4.99 and N 4.08 %.

Comment [AJB]: How?

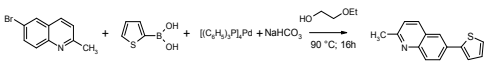
b) Preparation of 1,4-[Bis(6,6'-pyrenyl-2,2'quinolin-2-yl)vinyl)] benzene



A mixture of 6-pyrenyl-2-methylquinoline (3.0 g; 9.1 mmol) and terephthaldicarboxaldehyde (0.61 g; 4.5 mmol) was refluxed in acetic anhydride (20 ml) for 18 h and allowed to cool to room temperature. Methanol (25 ml) was added to the yellowish-green reaction mixture and the product filtered off under suction. The filter cake was washed thoroughly with methanol, de-ionised water, diethyl ether and finally with methanol. The product was dried under vacuum at 80 °C. Yield 2.9 g (83 %). The product further purified by sublimation. Mp 266 °C (DSC, onset), 282 (DSC, peak). T_g 74 °C. Elemental analysis, Found, C 91.55, H 4.89, N 3.44 %. $C_{60}H_{36}N_2$ requires, C 91.81, H 4.62 and N 3.57 %. Fluorescence (chloroform): λ_{max} (emission): 438 nm, excitation wavelength: 350 nm. Fluorescence (powder): λ_{max} (emission): 484 nm, excitation wavelength: 340 nm. Fluorescence (thin film): λ_{max} (emission): 466 (sh) and 494 nm, UV-Vis (chloroform) λ_{max} (absorption)/nm (ε)/$M^{-1}cm^{-1}$: 247 (8,220), 283 (75,151) and 328 (55,720) and 364 (69,886) . UV-Vis (thin film) λ_{max} (absorption)/nm: 239, 285, 336 and 363 nm. TGA/°C (weight loss %): 400 (3), Optical band gap: 2.9 eV.

Synthesis of E278-Th-ST

a) Preparation of 2-methyl-6-(2-thienyl)quinoline

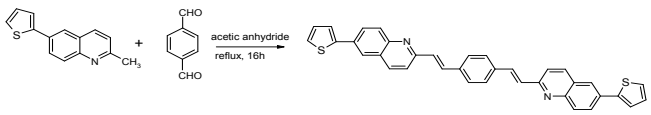


To a solution 6-bromo-2-methylquinoline (17.4g; 0.078mol) in 2-ethoxyethanol (100 ml) was added tetrakis(triphenylphosphine)palladium (2.7 g; 0.0023mol) and the reaction mixture was stirred at room temperature under nitrogen atmosphere for 5 minutes. 2-Thienylboronic acid (10.0g; 0.078mol) was added followed by ethoxyethanol (70 ml). Sodium hydrogencarbonate (20 g; 0.24mol) in water (100 ml) was then added and the reaction mixture was magnetically stirred and heated under nitrogen at 90 °C for 16 h. The cooled reaction mixture was filtered through a pad of Celite hyflo supercel and then extracted with dichloromethane (2 x 150 ml), after addition of de-ionised water. The organic layer was washed with brine, dried over anhydrous magnesium sulphate and the solvent removed to give a light brown liquid. The liquid was distilled under reduced pressure to remove ethoxy ethanol. The residue was triturated with diethyl ether and cooled in the refrigerator to give an off white solid, 10.6 g (61 %); Mp 87 °C (DSC, onset). Anal: Found; C 74.72, H 4.92, N 6.12 and S 13.43 %. $C_{14}H_{11}NS$ requires, C 74.63, H 4.92, N 6.21 and S 14.24 %.

Comment [AJB]: ??

Comment [AJB]: How?

b) Preparation of 1, 4-[Bis(6,6'-(2-thienyl)-2,2'quinolin-2-yl)vinyl)]benzene



A mixture of 2-methyl-6-(2-thienyl)quinoline (10.25 g; 0.046 mole) and terephthaldicarboxaldehyde (3.1; 0.023 mole) was refluxed in acetic anhydride (35 ml) for 18 h. The reaction mixture was allowed to cool to room temperature and methanol (50 ml) was added. A yellow-green solid separated out. The solid was filtered off under suction and the filter cake was washed thoroughly with methanol, de-ionised water, again with methanol and finally with diethyl ether. The product was dried under vacuum at 75 °C, Yield 9.5 g; (76 %). Mp 330 °C (DSC, onset). The product was purified by sublimation. Elemental analysis: Found, C 78.68, H 4.49, N 4.93, S 11.71 %, $C_{36}H_{24}N_2S_2$ requires, C 78.80, H 4.41, N 5.10 and S 11.69 %. Fluorescence (chloroform): λ_{max} (emission): 437 and 460(sh) nm, excitation wavelength: 400 nm. Fluorescence (powder): λ_{max} (emission): 501 nm, excitation wavelength: 340 nm. Fluorescence (thin film): λ_{max} (emission): 580 nm, UV-Vis (chloroform) λ_{max} (absorption)/nm (ε)/$M^{-1}cm^{-1}$: 280 (2417) and 403 (3901). UV-Vis (thin film) λ_{max} (absorption)/nm: 390 nm. TGA/°C (weight loss %): 400 (0), Optical band gap: 2.6 eV.