Supplementary Material (ESI) for Chemical Communications

S-heterocyclic annelated perylene bisimide: synthesis and co-crystal with Pyrene

Hualei Qian, Caiming Liu, Zhaohui Wang* and Daoben Zhu*

Beijing National Laboratory for Molecular Sciences, Key Laboratory of Organic Solids, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, P. R. China

Material and Methods

All chemicals were purchased from commercial suppliers and used without further purification unless otherwise specified. N,N'-Di(2,6-diisopropylphenyl)-3,4:9,10-perylenetetracarboxylic bisimide **1** was prepared according to known procedure.[1]

^{1}H NMR and ^{13}C NMR were obtained on a Bruker DMX 300 NMR Spectrometer and a Bruker ADVANCE 400 NMR Spectrometer. ^{1}H NMR chemical shifts are reported in ppm downfield from tetramethylsilane (TMS) reference using the residual protonated solvent as an internal standard. Mass spectra (MALDI-TOF-MS) were determined on a Bruker BIFLEX Ⅲ Mass Spectrometer.

Absorption spectra were measured with Hitachi (model U-3010) UV-Vis spectrophotometer, and fluorescene measurements were carried out with a Hitachi (model F-4500) spectrophotometer in a 1-cm quartz cell. The fluorescence quantum yield was determined by the optically dilute method with N,N'-Di(2,6-diisopropylphenyl)-3,4:9,10-perylenetetracarboxylic bisimide **1**[2] (Φ_f = 1.00 in $CHCl_3$) as reference. The X-ray diffraction data were collected on a Bruker SMART CCD area detector and a Rigaku Saturn CCD area detector.

Synthesis and characterization of compounds 4 and 5

N,N'-Di(2,6-diisopropylphenyl)-1,6,7,12-tetrachloroperylene-3,4:9,10-tetracarboxylic acid bisimide 4. A suspension of 1,6,7,12-tetrachloroperylene-3,4:9,10-tetracarboxylic acid bisanhydride (2.0g, 3.77mmol) and 2,6-diisopropylbenzenamine (3.3g, 18.85mmol) in 25ml propionic acid was stirred under reflux for 8 h. The mixture was neutralized with saturated $NaHCO_3$ solution. The solid was collected, washed, dried, yielded after column chromatography (silica gel, petroleum ether/CH_2Cl_2=1:1) 3.0g (95%) **4** as a orange-red solid.
^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.78 (s, 4H, perylene-H), 7.54 (t, 2H, phenyl), 7.39 (d, 4H, phenyl), 2.75 (m, 4H, isopropyl), 1.20 (d, 24H, isopropyl); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 161.3, 144.6, 134.6, 132.4, 130.7, 129.0, 127.9, 123.2, 122.9, 122.2, 28.6, 28.3, 23.0, 21.6, 13.1.

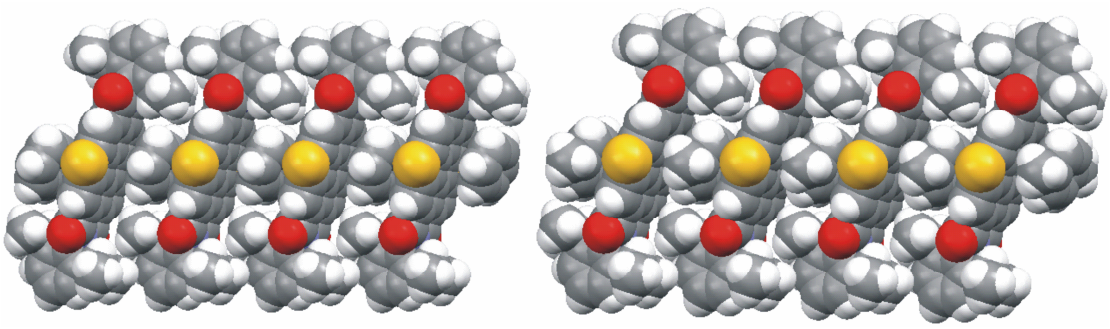
S-heterocyclic annelated perylene bisimide 5. $Pd(PPh_3)_4$ (0.42g, 0.49mmol) and $Bu_3SnSSnBu_3$ (2.22g, 3.63mmol) were added to a solution of compound **4** (1.54g, 1.81mmol) in toluene under a N_2 atmosphere. The mixture was refluxed for 10 hours. After removal of the solvent under vacuum, the crude was washed with EtOH, dried, dissolved in dichloromethane, and purified by column separation (silica gel, petroleum ether/CH_2Cl_2=1:1).Yield 1.00g (72%) **5** as an orange-yellow solid.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 9.63 (s, 4H, perylene-H), 7.54 (t, 2H, phenyl), 7.42 (d, 4H, phenyl), 2.89 (m, 4H, isopropyl), 1.22 (d, 24H, isopropyl); ^{13}C NMR (Cl_2ben, 75 MHz): δ = 166.0, 148.0, 143.3, 139.3, 130.8, 130.0, 128.2, 127.1, 125.9, 124.8, 122.2, 31.3, 29.8, 28.7, 25.9, 24.6, 23.1, 19.1, 15.4, 3.0; MS (MALDI-TOF): m/z (M^+) 771. Cal. 770.9.

1. (*a*) Y. Geerts, H. Quante, H. Platz, R. Mahrt, M. Hopmeier, A. Bohm and K. Müllen, *J. Mater. Chem.*, 1998, 8, 2357-2369; (*b*) H. Quante and K. Müllen, *Angew. Chem. Int. Ed. Engl.*, 1995, 34, 1323-1325.

2. C. You, R. Dobrawa, C. R. S. Möller and F. Würthner, *Top. Curr. Chem.*, 2005, **258**, 39-82.

X-ray crystallography



(a) (b)

Figure 1. Space-filling diagram of **5·Ph** (*a*) and **5·PhMe** (*b*)