Electronic Supplementary Information for

The lower rather than higher density charge carrier determines the NH_3-sensing nature and sensitivity of ambipolar organic semiconductors

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Content List

1. Chemicals and Characterization

Bis(phthalocyaninato) rare earth(III) complexes **1-4** were synthesized according to previously published procedure.[1] All other reagents and solvents were of reagent grade and used as received.

Electrochemical measurements were conducted using a CHI760D voltammetric analyzer based on the procedure reported previously.[2] The aggregates were fabricated using the QLS method following previously published process,[3] which were transferred onto the quartz substrate for UV-vis absorption spectra measurement and onto the bare SiO_2/Si substrate for X-ray diffraction (XRD), ultraviolet photoelectron spectrometry (UPS), and atomic force microscope (AFM) measurements. Electronic absorption spectra were recorded on a Hitachi U-4100 spectrophotometer. XRD experiments were carried out on a Rigaku D/max-B X-ray diffractometer with copper (Ka) radiation (λ = 1.5406 Å). UPS measurements were performed using a HeIα (21.22 eV) discharge lamp in a VG ESCALAB 220i-XL UHV photoelectron spectroscopy system which consists of an analysis chamber interconnected to a preparation chamber. AFM images were collected under ambient conditions using the tapping mode with a NanoscopeIII/Bioscope scanning probe microscope from digital instruments.

2. Electrical measurements and Gas sources for sensing experiments

OFET devices were fabricated from the aggregates **1-4** in the typical top-contact/bottom-gate geometry on the hexamethyldisilazane (HMDS)-treated doped-Si/SiO_2 (300 nm thickness, capacitance C_0=10 nF cm^{-2}) substrates, in which the source and drain gold electrodes are vacuum-deposited on the top of the aggregates employing a shadow mask.[4] The drain-source current (I_{ds}) versus drain-source voltage (V_{ds}) characteristic was obtained with a Hewlett–Packard (HP) 4140B parameter analyzer at room temperature. Experimental data were analyzed using standard field-effect transistor equations reported previously.[5] The direct current–voltage (I–V) measurements for the aggregats of **1-4** deposited on insulating SiO_2 substrates with the ITO interdigitated electrodes were performed using a Keithley 6517 electrometer with an incorporated DC voltage supply. The NH_3-sensing properties of samples **1-4** have been examined by exposing the corresponding aggregats to different concentrations of ammonia and measuring the current changes of the aggregats at a constantly polarized voltage of 5 V.

The desired ammonia concentration was produced by diluting a mixture NH_3/Ar (1000 ppm NH_3, from Air Liquid, France) with dry Ar using two mass flow controllers (total mass flow: 0.5 L min^{-1}).

Reference

1 G. Lu, M. Bai, R. Li, X. Zhang, C. Ma, P.-C. Lo, D. K. P. Ng and J. Jiang, *Eur. J. Inorg. Chem.*, 2006, **18**, 3703.
2 D. Gao, X. Zhang, X. Kong, Y. Chen and J. Jiang, *ACS Appl. Mater. Interfaces*, 2015, **7**, 2486.
3 Y. Chen, M. Bouvet, T. Sizun, Y. Gao, C. Plassard, E. Lesniewska and J. Jiang, *Phys. Chem. Chem. Phys.*, 2010, **12**, 12851.
4 Y. Chen, W. Su, J. Jiang, X. Li and Y. Liu, *J. Am. Chem. Soc.*, 2005, **127**, 15700.
5 S. M. Sze, *In Physics of Semiconductor Devices*, John Wiley &Sons, New York, 1981.

3. Figs. S1-S2 and Table S1

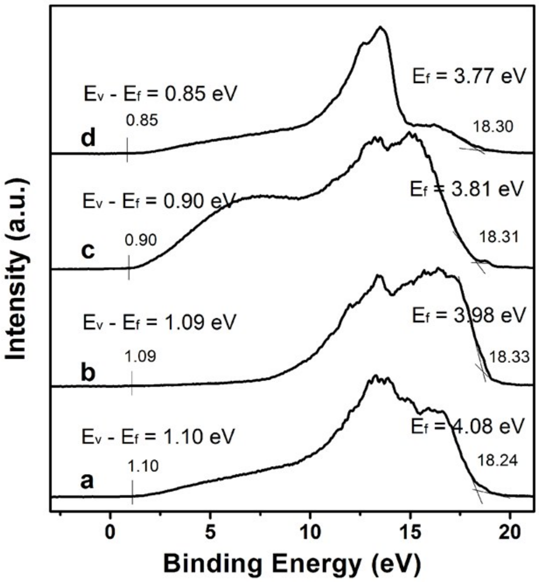

Fig. S1 UPS spectra (UV excitation by HeIα=21.22 eV) of the aggregates **1-4** (a-d). The Fermi level was obtained using the formula $E_f = hv - (E_{cut\text{-}off}^{max} – E_{cut\text{-}off}^{min})$. The minimum kinetic energy $E_{cut\text{-}off}^{min}$ at the left-hand part ($E_{cut\text{-}off}^{min} = E_v – E_f = E_{HOMO} – E_f$), corresponds to electrons from the HOMO level.

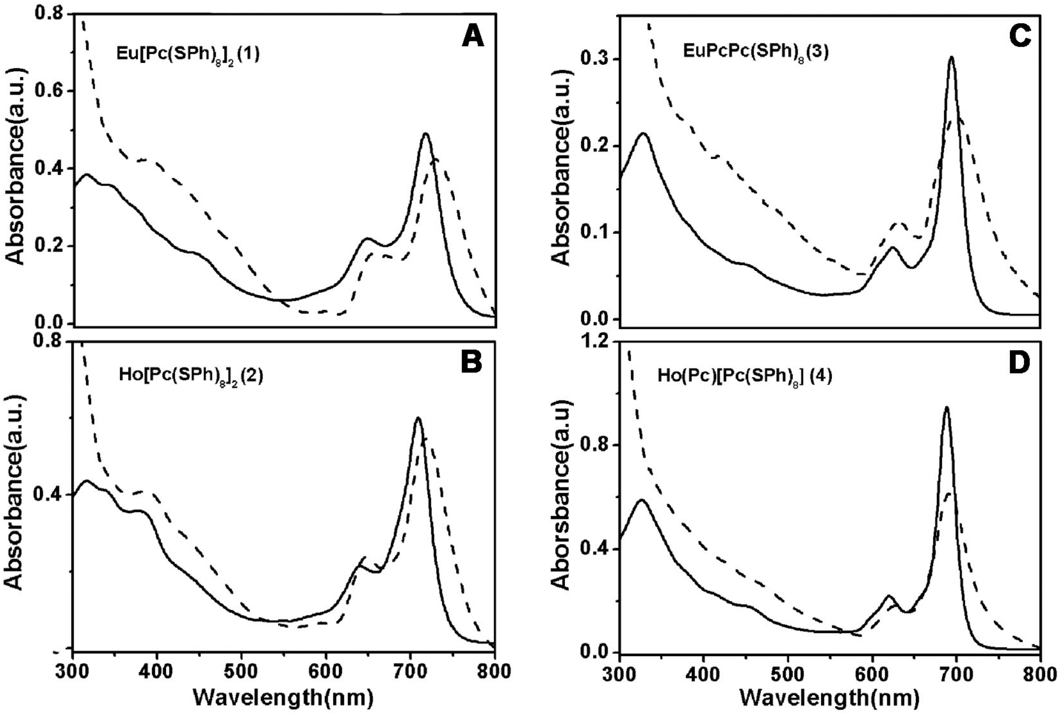

Fig. S2 UV-vis absorption spectra of **1-4** in CH_2Cl_2 solution (solid line) and self-assembled aggregates (dash line).

Table S1. Half-wave redox potentials of **1-4** (V *vs*. SCE) in CH_2Cl_2 containing 0.1 M TBAP (Tetrabutylammonium perruthenate) and maximum Q band absorption of compounds **1-4** in CH_2Cl_2 solution and self-assembled nanostructures.

Compound	E_{Oxd1}	E_{Red1}	E_{Red2}	E_{Red3}	$\Delta E^{o}_{1/2}$ [a]	$\Delta E^{o\prime}_{1/2}$ [a]	LUMO/eV[b]	HOMO/eV[b]	$\Delta\lambda_{max}$/nm		$\Delta\lambda_{max}$/nm[c]
									solution	aggregate	
1	+0.67	+0.30	-0.84	-1.08	0.37	1.14	-3.60	-4.74	716	730	14
2[d]	+0.66	+0.28	-0.85	-1.04	0.38	1.13	-3.59	-4.72	709	719	10
3	+0.64	+0.22	-0.90	-1.25	0.42	1.12	-3.54	-4.66	694	702	8
4[d]	+ 0.58	+0.17	-0.92	-1.21	0.41	1.09	-3.52	-4.61	688	691	3

[a] $\Delta E^{o}_{1/2} = E_{Oxd1} - E_{Red1}$, $\Delta E^{o\prime}_{1/2} = E_{Red1} - E_{Red2}$;

[b] HOMO (eV) = – 4.44eV – e E_{Red1}, LUMO (eV) = – 4.44eV – e E_{Red2};

[c] $\Delta\lambda_{max} = \lambda_{max(aggregate)} - \lambda_{max(solution)}$;

[d] Cited from G. Lu, M. Bai, R. Li, X. Zhang, C. Ma, P.-C. Lo, D. K. P. Ng and J. Jiang, *Eur. J. Inorg. Chem.,* 2006, **18**, 3703.