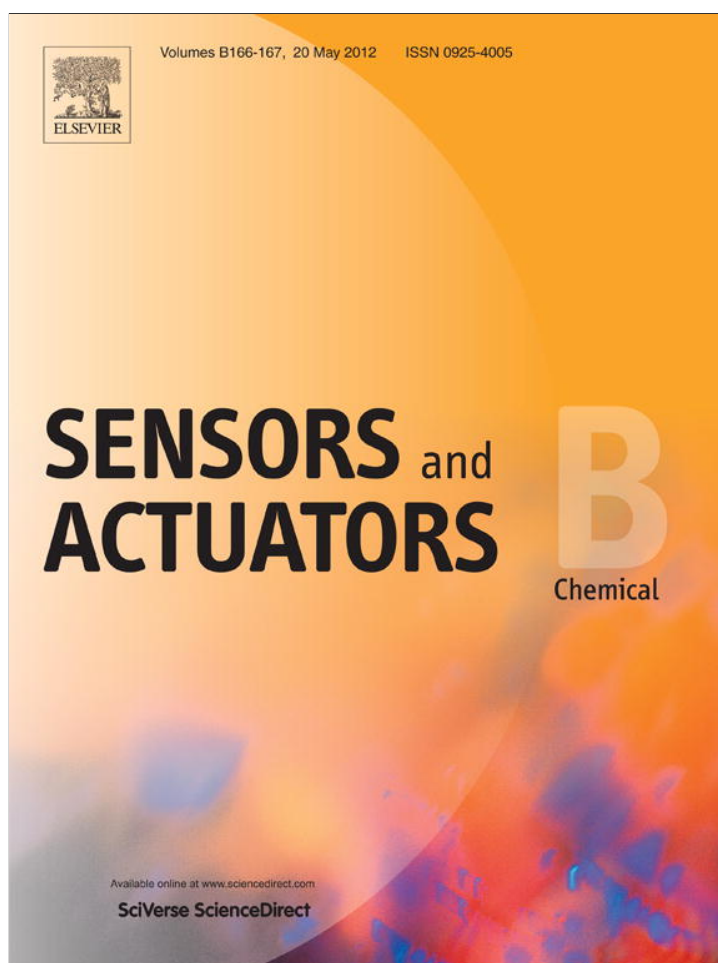


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Solution-processed thin films based on sandwich-type mixed (phthalocyaninato)(porphyrinato) europium triple-deckers: Structures and comparative performances in ammonia sensing

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ABSTRACT

The solution-processed thin films of a series of three sandwich-type mixed (phthalocyaninato)(porphyrinato) europium complexes with different numbers of hydroxyl groups at the meso-substituted phenyl groups of porphyrin ligand **1–3** were prepared by a quasi-Langmuir–Shäfer (QLS) method. Examination by spectroscopic methods revealed that *J*-type aggregates have been formed with the increasing degree of order of molecular stacking **1** < **2** < **3** films. The IR and XRD results reveal that, a dimeric supramolecular structure was formed depending mainly on the π – π interaction between the tetrapyrrole cores of neighboring triple-decker molecules, which, as the building blocks, self-assembled into the target nanostructures through intermolecular hydrogen bonds. Competition and cooperation between the intermolecular π – π interaction and hydrogen bonding for different compounds were revealed to result in thin-film microstructure with a different morphology from nano-grains for **1** and **2** and nano-sheets for **3**. An increasing sensitivity to NH₃ at varied concentrations in the range of 15–800 ppm, follows the order **3** < **1** < **2**, revealing the effect of film structure/morphology on sensing performance. In particular, excellent sensitivity, nearly complete reversibility and reproducibility to NH₃ even at room temperature are obtained for the ultra-thin solution processed films from **2**.

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1. Introduction

Thin films of organic materials having semiconducting properties are being extensively studied due to the very promising applications of organic electronics [1]. As the typical representative of functional molecular materials with large conjugated electronic structure, phthalocyanines have been intensively studied as good molecular semiconductor materials due to their large conjugated π system, unique electronic characteristics, high thermal and chemical stability [2]. In addition, phthalocyanines, both metalated (MPcs; M = p-, d-, and f-block elements) and metal-free (H₂Pc), are organic p-type semiconductors that are used as chemiresistive gas sensors [3]. MPC conductivities are increased by oxidant gases that generate charge carriers (holes) and are decreased by electron-donating gases which trap charge carriers [4–8]. It is worth noting that most of the devices based on phthalocyanines have been fabricated by vacuum sublimation.

From the early nineties, solution-based thin-film deposition [spin coating, molecular assemblies, and Langmuir–Blodgett (LB)] [9–13] methods have been attracting increasing research interest, as it has been recognized that organic semiconductors can compete with their inorganic counterparts only when low-cost fabrication methods such as solution deposition or printing techniques are available [14]. Moreover, it is well-known that sandwich phthalocyaninato and/or porphyrinato metal triple-decker complexes are more soluble in common organic solvents and therefore have good film-forming behavior. In addition, with a special sandwich structure and extended π networks along the axis perpendicular to the macrocycle plane [15–19], this class of molecular materials are expected to play a more important part in gas sensing applications [20–22] as well as in information storage [23] and organic field-effect transistors [24–26] compared with their monomeric counterparts. Very recently, the solution-processed thin solid films of an amphiphilic tris(phthalocyaninato) rare earth triple-decker, Eu₂[Pc(15C5)₄]₂[Pc(OC₁₀H₂₁)₈], have been revealed to display excellent sensitive, stable and reproducible responses to oxidizing gas, O₃ [21]. However, reports on the gas sensing behavior to reducing gas such as ammonia from this class of complexes

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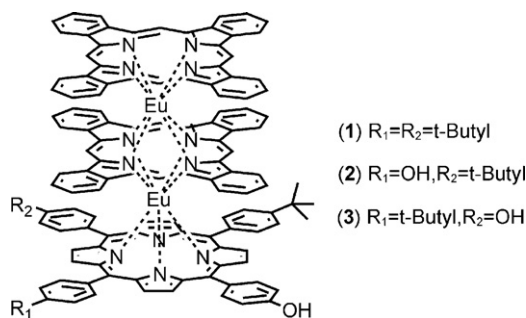


Fig. 1. Schematic molecular structures of $\text{Eu}_2(\text{Pc})_2[\text{T}(\text{OH})\text{PP}]$ (**1**), $\text{Eu}_2(\text{Pc})_2[\text{cis-T}(\text{OH})_2\text{PP}]$ (**2**) and $\text{Eu}_2(\text{Pc})_2[\text{trans-T}(\text{OH})_2\text{PP}]$ (**3**).

prepared via solution methods are still rare [20]. In the present study, we describe the fabrication of thin-film chemiresistors by employing a simple *quasi-Langmuir–Shäfer* (QLS) method from three sandwich-type mixed (phthalocyaninato)(porphyrinato) europium triple-decker complexes with different numbers of hydroxyl groups at the meso-substituted phenyl groups of porphyrin ligand, labeled $\text{Eu}_2(\text{Pc})_2[\text{T}(\text{OH})\text{PP}]$ [$\text{Pc} = \text{dianion of phthalocyanine, T}(\text{OH})\text{PP} = \text{dianion of 5-(4-droxyphenyl)-10,15,20-tris(4-tert-butylphenyl)porphyrin}$] (**1**), $\text{Eu}_2(\text{Pc})_2[\text{cis-T}(\text{OH})_2\text{PP}]$ [$\text{cis-T}(\text{OH})_2\text{PP}$ dianion of 5,10-di(4-hydroxyphenyl)-15,20-di(4-tert-butylphenyl)porphyrin] (**2**) and $\text{Eu}_2(\text{Pc})_2[\text{trans-T}(\text{OH})_2\text{PP}]$ [$\text{trans-T}(\text{OH})_2\text{PP}$ dianion of 5,15-di(4-hydroxyphenyl)-10,20-di(4-tert-butylphenyl)porphyrin] (**3**) (Fig. 1). The QLS films of **1–3** were thoroughly characterized by spectroscopic methods, atomic force microscopy (AFM) observation and current–voltage (I – V) measurements. The successive exposure of the active layers of **1–3** to NH_3 gas within the part per million range, at room temperature, is examined and highly sensitive, stable and reproducible responses of active layers to NH_3 gas are obtained and compared. Competition and cooperation between the intermolecular π – π interaction and hydrogen bonding for different compounds were revealed to result in thin-film microstructure with a different morphology, which strongly influence their I – V and gas sensor characteristics. The present work, representing our continuous efforts in understanding the relationship between the film structure, morphology and gas sensor performance of tetrapyrrole organic semiconductors [21,27,28], will be helpful for attracting further research interests in the field of chemical sensors and the semiconducting properties of phthalocyanine derivatives, in particular triple-decker mixed (phthalocyaninato)(porphyrinato) rare earth complexes for sensor applications.

2. Experimental

2.1. Materials and chemicals

The sandwich mixed (phthalocyaninato)(porphyrinato) rare earth triple-decker complexes, $\text{Eu}_2(\text{Pc})_2[\text{cis-T}(\text{OH})_2\text{PP}]$ (**1**), $\text{Eu}_2(\text{Pc})_2[\text{T}(\text{OH})\text{PP}]$ (**2**) and $\text{Eu}_2(\text{Pc})_2[\text{trans-T}(\text{OH})_2\text{PP}]$ (**3**), were used as synthesized previously [29]. All other reagents and solvents were of reagent grade and used as received.

2.2. Thin film deposition

The nanostructures of compounds **1**, **2** and **3** were fabricated by using the solution-based method named *quasi-Langmuir–Shäfer* (QLS) according to the following procedure [21]. Briefly, 4.0 mL of chloroform solution (0.30 mg mL^{-1}) was put into a cylindrical glass container (ca. 24 cm^3 internal volume), then 2 mL water was slowly added onto the surface of the solution, while chloroform solution surface of the sample was incompletely covered by water. During

CHCl_3 solvent evaporation, organic molecules gradually assembled to form some fine nanostructures at the $\text{CHCl}_3/\text{water}$ interface. After complete evaporation of CHCl_3 , the densely packed film remained on the water surface. After carefully adding more water into the container, the film can be easily transferred by horizontal lifting from the water surface onto the glass and ITO/glass interdigitated electrodes. The process was repeated to obtain the required number of layers. Residual water on the substrates, between transfer steps and after the final transfer, was removed with a stream of argon. It should be noted that, prior to the deposition, substrates were successively sonicated in dichloromethane, methanol and distilled water and dried with argon gas. In present case, 15-layer QLS films of **1–3** are obtained for I – V and sensing experiments, respectively.

2.3. Characterization

Electronic absorption spectra were recorded on a Hitachi U-4100 UV–visible spectrophotometer. Fourier transform infrared (FTIR) spectra were recorded using a Bruker Vertex 70 infrared spectrometer with 2 cm^{-1} resolution. X-ray diffraction (XRD) experiments were carried out on Rigaku D/max- γB X-ray diffractometer with copper ($K\alpha$) radiation. AFM images were collected in air under ambient conditions using the tapping mode with a Nanoscope IV/Bioscope scanning probe microscope from Digital instruments.

2.4. Electrical measurements

The fundamental electrical and sensor measurements were performed using a Keithley 6517 electrometer with an incorporated DC voltage supply, always at room temperature in the range 22 – 25°C . The electrometer is controlled by self-made software via the GP-IB board. Current–voltage (I – V) curves were registered in the -10 to 10 V voltage range with 1 V increments, starting and finishing at 0 V bias to avoid irreversible polarization effects. On the other hand, the NH_3 -sensing properties of samples have been examined by exposing the corresponding films to different concentrations of ammonia and measuring the current changes of the films at a constantly polarized voltage of 5 V . All experiments have been conducted at least twice to ensure reproducibility.

The interdigitated array electrode is composed of 10 pairs of ITO electrode digits (fingers) deposited onto a glass substrate with the following dimensions: $125\text{-}\mu\text{m}$ electrode width, $75\text{-}\mu\text{m}$ spacing, $5850\text{-}\mu\text{m}$ overlapping length, and 20-nm electrode thickness. Conductivity, σ , can be calculated by the following equation,

$$\sigma = \frac{dI}{(2n-1)LhV} \quad (1)$$

where d is the interelectrode spacing, I the current, n the number of electrode digits, L the overlapping length of the electrodes, and h the electrode thickness as the film thickness exceeds that of the ITO electrodes in present case. For the results reported here, a dc voltage of 5.0 V was used. Ohmic behavior was observed in this voltage range.

2.5. Gas sources for sensing experiments

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}). The maximum water contents in ammonia and argon cylinders purchased were 100 ppm and 2 ppm , respectively.

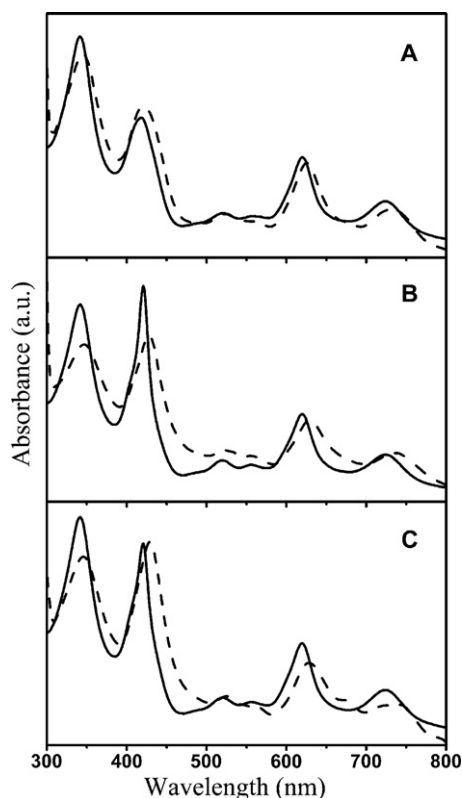


Fig. 2. Electronic absorption spectra of compounds 1–3 (A–C) in solution (solid line) and the QLS films (dashed line).

3. Results and discussion

3.1. Electronic absorption spectra

To gain insight into the molecular packing of the mixed triple-decker complexes 1–3, electronic absorption spectra of 1–3 in chloroform solution and the QLS films were recorded, Fig. 2, and the corresponding data are compiled in Table S1 (Supporting Information). In line with those of analogous $M_2(\text{Pc})_2(\text{TCIPP})$ ($M = \text{Nd}, \text{Gd}, \text{Dy}$) [30], all three of these triple-decker complexes dissolved in CHCl_3 exhibited the absorptions at 342 and 418–421 nm, which can be attributed to the phthalocyanine and porphyrin Soret bands, respectively, while the strong absorptions at 620 and 724 nm can be attributed to their Q bands [29]. In QLS films of 1–3, all the Soret and Q-bands of three triple-decker complexes were broadened and red-shifted as compared to those in solution, which can be ascribed to the formation of *J*-type aggregates, suggesting effective intermolecular interactions between the neighboring triple-decker molecules [29]. In addition, a comparison for the electronic spectra of 1 and 2 (or 3) in QLS films indicates that, along with the increase of hydroxyl number in the meso-substituted phenyl groups of porphyrin ligand, both the phthalocyanine and porphyrin Soret and Q bands continuously shift to the lower energy side in the same order, revealing the effect of the hydrogen-bonding interaction among hydroxyl groups on tuning the intermolecular interaction of triple-decker molecules. Furthermore, comparison in the film electronic absorption spectra between 2 and 3, with two hydroxyl groups at two neighboring and opposite meso-substituted phenyl groups of porphyrin ring, respectively, reveals the effect of hydroxyl positions on tuning the intermolecular interaction in the aggregate due to the directional-specific character of hydrogen bonding. Obviously, the stronger intermolecular interactions in films of 3 and 2 than that of 1 should be attributed to the higher level of order packing

of molecules in the films of 3 and 2, which is confirmed by the XRD and AFM experimental results as detailed below.

3.2. FTIR spectra

The FTIR spectra of the QLS films of 1–3 obtained are shown in Fig. S1 (Supporting Information). In the FTIR spectra of triple-deckers 1–3, one relatively broad band appearing in the range $3293\text{--}3338\text{ cm}^{-1}$ are assigned to the hydrogen bonding stretching vibration [31,32]. This is in line with the X-ray diffraction (XRD) result as detailed below, indicating the significant effect of the hydrogen-bonding interaction on the formation of the QLS films of 1–3.

3.3. X-ray diffraction

The quality of the QLS films of compounds 1–3 has been further assessed using X-ray diffraction (XRD) technique. As shown in Fig. 3A, in the low angle range, the XRD diagram of the QLS films of 1 shows three diffraction peaks at $2\theta = 5.64^\circ$ (corresponding to 1.57 nm), 6.16° (1.43 nm), and 6.78° (1.30 nm), respectively, which are ascribed to the diffractions from the (1 0 0), (0 1 0), and (0 0 1) planes [29,33]. These diffraction results could be assigned to the diffractions from a parallelepipedal lattice with cell parameters of $a = 1.57\text{ nm}$, $b = 1.43\text{ nm}$ and $c = 1.30\text{ nm}$. It is worth noting that, in the wide angle region, the XRD pattern presents two sharp reflections at 0.32 and 0.24 nm, respectively, which can be attributed to the π – π stacking between tetrapyrrole cores of neighboring triple-decker molecules and the distance of the hydrogen-bonding interaction among hydroxyl groups [29,34]. Combining these XRD data with the single crystal X-ray analysis of $\text{Eu}_2(\text{Pc})_2(\text{TCIPP})$ [35], one may propose, during the molecular self-assembly process of this compound, that a dimeric supramolecular structure was formed depending mainly on the π – π interaction between the tetrapyrrole cores of neighboring triple-decker molecules, which as the building block further self-assembled through an intermolecular hydrogen bond between two triple-decker molecules with an edge-to-edge ordering into the target nanostructures. One unit consisting of two triple-decker molecules is given for compound 1, Fig. 3D. This seems also true for triple-deckers 2 and 3. The XRD pattern of QLS films of 2 and 3 shows a well-defined peak at 1.62 and 2.30 nm, respectively, Fig. 3B and C. This corresponds with the (1 0 0) reflection of nanostructures of compound 1 appearing at 1.57 nm. The increase of this lattice constant in the order of 1, 2, and 3 indicates the increasing effect of the hydrogen bonding interaction between dimers on the formation of aggregate of these complexes in the same order, Fig. 3E and F. Obviously, in the self-assembled nanostructures with long range periodicity along the (0 1 0) direction as revealed for triple-deckers 2 and 3, the lattice parameter in this direction decreases from 1.39 nm for 2, and to 1.33 nm for 3, which is less than that of 1 (1.43 nm), suggesting that the inter-molecular π – π interaction between triple-decker molecules gradually gets increase in the same order. This is in line with the conclusion resulted from the electronic absorption spectroscopic properties as detailed above. It is worth noting that, for compound 3 with two hydroxyl groups attached at the opposite meso-substituted phenyl groups of porphyrin ligand, the (0 0 1) diffraction observed at 1.30 and 1.28 nm for the nanostructures of 1 and 2 respectively was absent. As a consequence, growth in this direction during the self-assembly process is limited or prohibited. However, one second-order diffraction from the (2 0 0) plane was found at 1.09 nm for the nanostructures of 3, suggesting the existence of long-range periodicity along this direction in the self-assembled nanostructures of this triple-decker complex, likely due to the efficient hydrogen bonding between dimers from the two

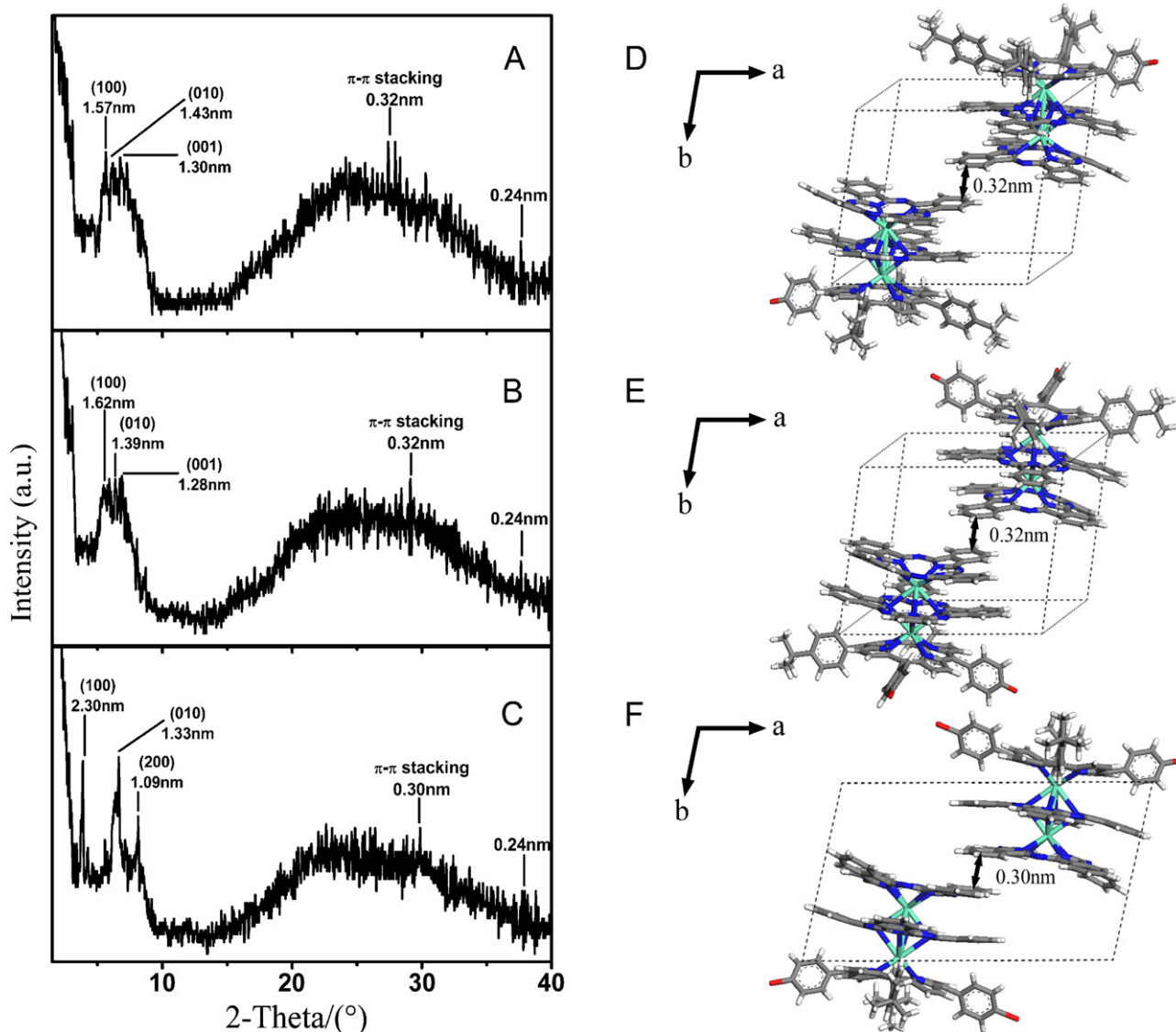


Fig. 3. X-ray diffraction patterns of the QLS films of compounds **1–3** (A–C) and schematic representation of the unit cell in the QLS films of **1–3** (D–F).

hydroxyl groups attached at the opposite meso-substituted phenyl groups of porphyrin ligand.

3.4. AFM surface topography

AFM provided information on the aspect of the films and allowed us to correlate the morphology and electrical and gas sensing properties. Fig. 4A exhibits the surface topography of the QLS films picked up by **1** onto glass substrate. The surface of QLS films of **1** consisted of a granular structure with an average diameter of approximately 100 nm giving a root mean square (rms) roughness value of 2.866 nm, indicating a smooth film structure covering the glass substrate. The further increase in the number of the hydroxyl groups at the neighboring meso-substituted phenyl group of the porphyrin ring in the triple-decker molecules induces the formation of a relatively uniform self-assembled nanostructures (approximately spherical shape) with a large average diameter of ~120 nm and rms roughness value of 1.599 nm for the QLS films of **2**, Fig. 4B. The increase in the domain size and decrease rms for **2** compared to that of **1** would reduce the boundaries and carrier traps in the film and usually have a stabilizing effect on their electrical properties [36] and enhance their sensing abilities and recovery

rates [37,38]. In the case of **3**, the films exhibit an unusual sheet-like surface morphology with ca. 500 nm in width (Fig. 4C), consistent with the unique XRD pattern also observed. The rms roughness value is about 2.485 nm. This morphology can be attributed to the introduction of an additional hydroxyl group at the opposite position, which provides another growing direction for the aggregates along the direction of unlimited intermolecular hydrogen bonding besides the π - π interaction direction. These results reveal that the hydrogen bonding interaction in addition to the π - π stacking between neighboring molecules plays an important role in controlling and tuning the morphology of aggregates (nanostructures) of these triple-decker compounds via tuning the intermolecular interaction.

3.5. Current–voltage (I - V) characteristics

To ensure that all the devices had good electrical contact to the electrodes, the I - V curves were measured (Fig. 5). All devices exhibit similar Ohmic behavior at low bias voltages. However, the response increases in the order $1 < 2 \ll 3$ film, which could be indicative of subtle thin film microstructure/morphology/crystal packing effects that modulate atmospheric charge carrier trap penetration into the

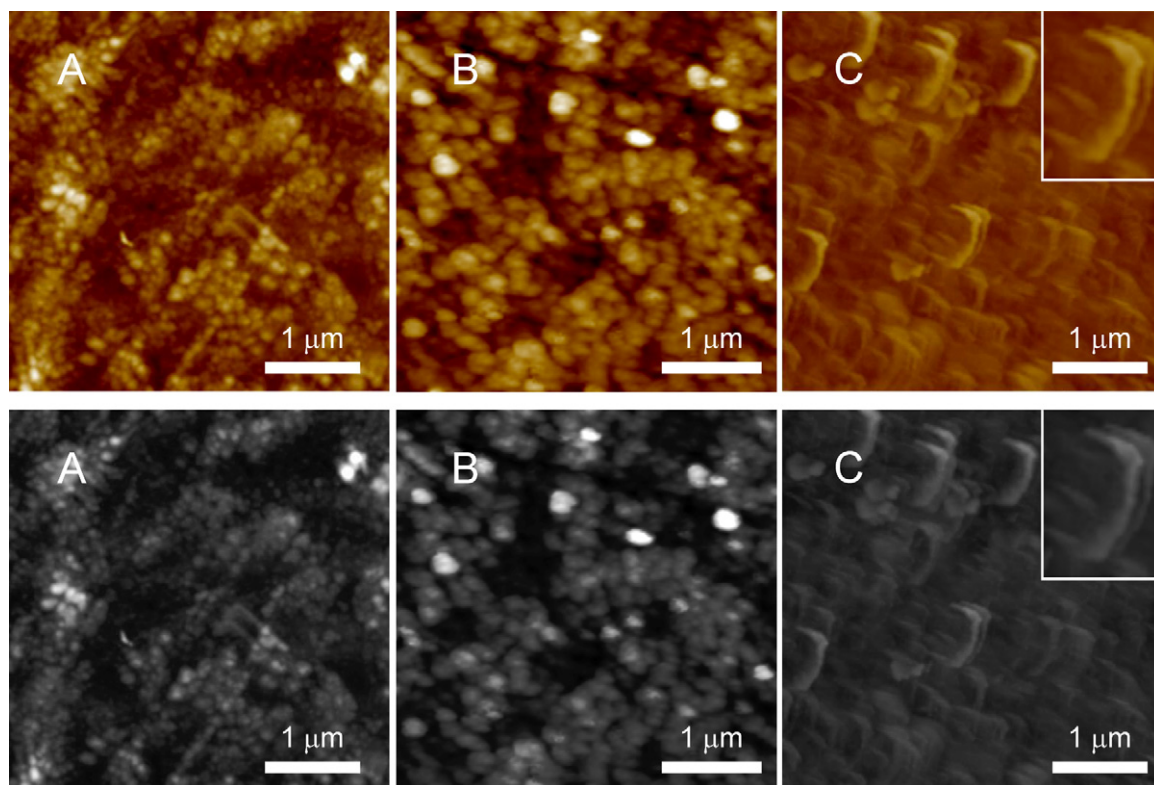


Fig. 4. AFM images of the QLS films of compounds 1–3 (A–C). The insert one is a magnified image of nanosheets of compound 3.

semiconductor thin films. We estimated using Eq. (1) electronic conductivity σ of 1.22×10^{-6} and $3.02 \times 10^{-6} \text{ S cm}^{-1}$ for the QLS films of 1 and 2, respectively. For the QLS films of 3, the value is $3.59 \times 10^{-5} \text{ S cm}^{-1}$, which is the largest in the QLS films of this class of materials. In light of the previous observations, and as reported in the literature with regard to electrical characterization of MPCs compounds [21,39,40]: higher is the order of a densely packed molecular architecture in the film matrix, higher is the mobility of charge carriers, resulting in a higher current passed through the devices.

3.6. Responses of the devices to NH_3

The QLS films of compounds 1–3 are all p-type semiconductors. Upon exposure to the electron-donating NH_3 gas, the hole concentration near the surface will be weakened since NH_3 traps majority charge carriers, resulting in the decrease in conductivity. Responses of the 1–3 sensors were determined from the time-dependent current plots when exposed to NH_3 (15–800 ppm) diluted in dry argon,

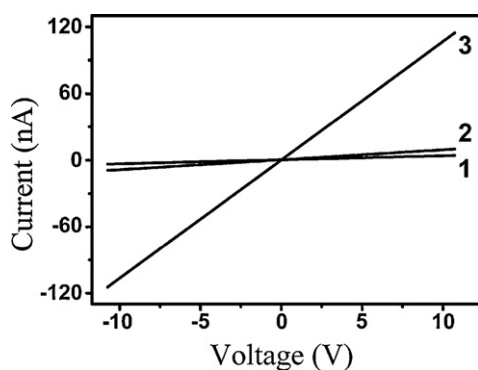


Fig. 5. Representative I – V characteristics of the QLS films of compounds 1–3.

at room temperature, Fig. 6. The sensing performances were studied with a duty cycle where the dynamic exposure period is fixed at 1 min and the static recovery period at 4 min. It can be seen qualitatively in Fig. 6, change in the current of the films of 2 clearly shows a comparatively better reversibility and reproducibility toward NH_3 at room temperature as compared to the films of both 1 and 3. The current drift at the end of the recovery period in the QLS films is 0.0073, 0.013, and 0.21 nA per cycle for complexes 1–3, i.e. 0.48%, 0.31% and 0.43% of current for the overall experiment. The most stable current was found for QLS films of 2. Moreover, in comparison with phthalocyanine-based ammonia sensor in our previous study [41], the QLS films of 2 in the present case has shown better stability and reproducibility evaluated from drift of current.

In order to quantitatively analyze the sensor responses, the percent current change was calculated for each concentration, as follows:

$$\% \text{ current change} = \left[\frac{I_o - I_f}{I_o} \right] \times 100 \quad (2)$$

where I_o is the current value at the beginning of an exposure/recovery cycle and I_f is the current value at the end of the 1 min exposure period. That value is designated as the sensor response. The sensor responses of the QLS films of 1–3 are all linear with respect to various concentrations of ammonia in the range of both 15–100 ppm and 200–800 ppm (Adj. R -square > 0.97), respectively (Fig. 7) [8]. Thus, such films can be used to quantitatively analyze the concentration of NH_3 . For the QLS films of 1–3, the slope (in % ppm $^{-1}$) of the linear fit of the percent current change as a function of NH_3 concentration, is about 0.014, 0.019 and 0.0072 in the range of 15–100 ppm, and 0.0046, 0.0082 and 0.0026 in the range of 200–800 ppm, respectively. An increasing sensitivity to NH_3 , at varied concentrations in the range of 15–800 ppm, follows the order 3 < 1 < 2, revealing the effect of both structures and morphologies of the QLS films on sensing performance. In particular,

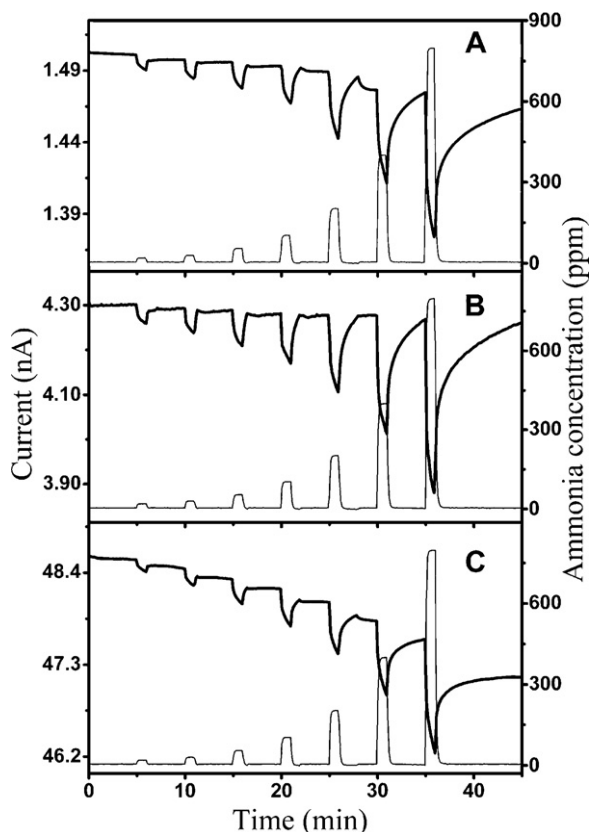


Fig. 6. The time-dependent current plots for the QLS films of compounds 1–3 (A–C) films exposed to NH₃ at varied concentration in the range of 15–800 ppm (exposure: 1 min, recovery: 4 min), while the bottom rectangular pulses for each current plot represent the NH₃ concentration as a function of time.

the time-dependent current plot of the QLS films of **2**, clearly shows an excellent separation of the different ammonia concentration levels and nearly complete reversibility and reproducibility even at room temperature, which is unique among the single component solution-processable organic semiconductor-based films as an ammonia sensor thus far reported in the literature [41–45]. The relatively uniform granular nanostructure with a densely packed molecular architecture and the lowest rms roughness value of the QLS films of **2** in this class of materials might directly contribute to the excellent sensing performance observed in our experiments. The lower sensitivity of largely sheet-like surface morphology of **3**, as compared to that of the small-granular one of **1** and **2**, can then be explained by the difference in the number of adsorption

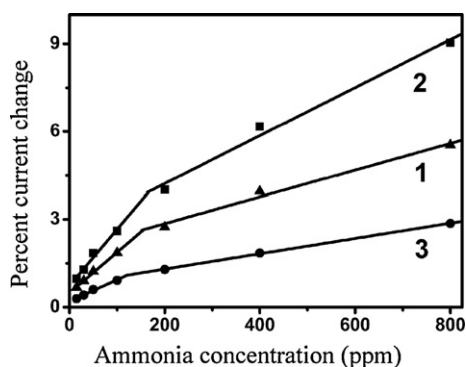


Fig. 7. Sensor response varies linearly with NH₃ concentration of the QLS films of compounds 1–3; slope (% ppm⁻¹, R² ≥ 0.97) for each may be used as a measure of sensor response.

sites. For the QLS films of **3**, continuity of the conductive path may be disrupted by a higher distribution of inter-space between the nanosheets containing structural defects (the inset of Fig. 4C), with much of the NH₃ molecules adsorbed on the films having little contributions to the conductivity [46], thus the %current change is much smaller than that of **1** and **2**. It is worth noting that, QLS films of **1–3** are more sensitive to low NH₃ concentration (15–100 ppm), which is important for the application as NH₃ sensor and/or detector. Indeed, it should be pointed out that, among pollutants, ammonia (NH₃) needs to be measured in the 10–100 ppm range when detected in industrial wastes control.

Furthermore, the absolute value of relative response for either **1** or **2** (with granular film morphology) during recovery period to each concentration is almost equal to that during exposure period, Fig. S2A and S2B (Supporting Information). However, a lower relative response for **3** (with distinctive sheet-like film morphology) during recovery period than exposure period has been observed in Fig. S2C (Supporting Information). This phenomena unambiguously indicates the reversibility, reproducibility and response for present sensors are all related to the film morphology.

3.7. Sensor response kinetics

First-order kinetics analysis as developed by Tongpool et al. has been used to model the kinetics of gas-MPC sensor interactions [47]. The response curves appear to follow a first-order decay process, the reaction rate, v , is

$$v = \frac{-d[A]}{dt} = k[A] \quad (3)$$

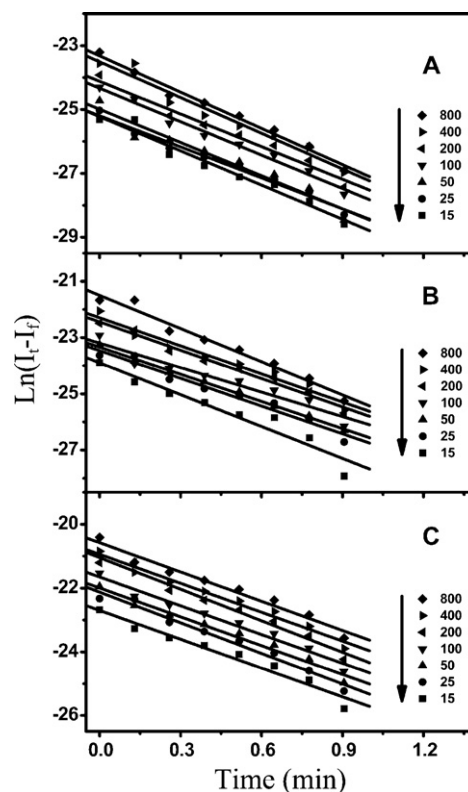


Fig. 8. The kinetics plots of compounds 1–3 (A–C) films: $\ln(I_t - I_f)$ versus time are predominantly linear for different concentrations of NH₃, suggesting first-order kinetics. Arrows indicate the direction of change with decreasing concentration of ammonia.

with k as the sensor response rate constant and $[A]$ as the concentration of species A . By integration, this equation becomes

$$\ln[A]_t = \ln[A]_0 - k[t - t_0] \quad (4)$$

where $[A]_0$ is the initial concentration of A and $[A]_t$ is the concentration of A at time t . This may be adapted to the sensors by defining $[A]_t$ as $(I_t - I_f)$ where I_t is the current at time t and I_f is the final current after an exposure period. Consequently, if the plot of $\ln(I_t - I_f)$ versus t is linear, the reaction is of the first order and the slope of the straight line is $-k$. Fig. 8 shows plots of $\ln(I_t - I_f)$ versus t for the QLS films of 1–3. Examination of these plots shows that the slope variation as a function of NH_3 concentration is almost similar for a given film. The average rate constant calculated from the slopes of kinetics plots for complexes 1–3 films is 3.52 min^{-1} , 3.49 min^{-1} and 3.09 min^{-1} , respectively. These data suggest that sensor adsorption mechanisms are similar for all QLS films of 1–3 [8].

4. Conclusions

The QLS films of a series of the amphiphilic sandwich mixed (phthalocyaninato)(porphyrinato) europium triple-deckers 1–3 have been prepared. Comparative investigation results reveal that competition and cooperation of intermolecular hydrogen bondings with the π – π interaction between tetrapyrrole rings in the triple-decker molecules leads to different molecular packing conformations and in turn different morphologies in self-assembled thin films, which strongly influence their I – V and gas sensor characteristics. The QLS films of 1–3 as chemiresistive sensors exhibited the good sensitivities to ammonia in the 15–800 ppm range and the sensor responses obey first-order kinetics. The relatively uniform granular nanostructure with a densely packed molecular architecture and the lowest rms roughness value of the QLS films of 2 shows an excellent separation of the different ammonia concentration levels and nearly complete reversibility and reproducibility even at room temperature. This sensor should have potential applications for measuring ammonia levels in chemical alarm systems. This study can open an interesting opportunity for the use of triple-decker heteroleptic analogs containing different tetrapyrrole ligands in particular those with mixed phthalocyaninato and porphyrinato ligands as sensitive materials deposited via solution processes.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.snb.2012.02.094.

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