Electronic supplementary information

Diverse sensor responses from two functionalized tris(phthalocyaninato) Europium ambipolar semiconductors towards three oxidative and reductive gases

Shanshan Liu, Haoyuan Wang, Xiangyang Wang, Shaoren Li, Heyuan Liu, Yanli Chen,* Xiyou Li*

* Corresponding Author

*E-mail: yanlichen@upc.edu.cn (Y. Chen) and xiyouli@upc.edu.cn (X. Li)
Caption of Content

**Fig. S1.** Experimental isotopic pattern for the molecular ion of compounds 1-2 shown in the MALDI-TOF mass spectrum.

**Fig. S2.** $^1$H NMR spectrum of compounds 1-2 in CDCl$_3$.

**Fig. S3.** The molecular dimension of compounds 1-2 obtained using PCMODEL for windows Version 6.0, Serena Software.

**Fig. S4.** Polarized UV-vis spectra of the LS films of 1-2.

**Fig. S5.** XRD pattern recorded in in-plane (grazing incidence) mode for the LS films of 1(A)-2(B).

**Fig. S6.** Output characteristics ($I_{ds}$ vs. $V_{ds}$) of ambipolar OFET device based on LS films of 1 (A-B) and 2 (C-D).

**Fig. S7.** The recovery time for 1-2 films exposed to NO$_2$ at varied concentration in the range of 0.1-0.85 ppm (exposure: 2 min).

**Fig. S8.** The time-dependent current evolution curves of the three toxic gases (H$_2$S, NH$_3$, and NO$_2$) in a sequential testing for LS films of 1(A) and (B).

**Fig. S9.** The response of the devices for compound 1(A)-2(B) under 0.45 ppm NO$_2$ exposure of 2 min and 10 min.

**Table S1.** The orientation angle of the phthalocyanine ring determined from polarized UV-vis absorbance of the LS films of compounds 1-2.

**Table S2.** The gate-induced sheet carrier densities ($n$) of the LS films of compounds 1-2.
**Fig. S1.** Experimental isotopic pattern for the molecular ion of 
Eu$_2$[Pc(OC$_8$H$_{17}$)$_8$][Pc(OCH$_2$CF$_3$)$_8$] (A) and Eu$_2${Pc[(OC$_2$H$_4$)$_3$OCH$_3$]$_8$}[Pc(OCH$_2$CF$_3$)$_8$] (B) shown in the MALDI-TOF mass spectrum.

**Fig. S2.** $^1$H NMR spectrum of Eu$_2$[Pc(OC$_8$H$_{17}$)$_8$][Pc(OCH$_2$CF$_3$)$_8$] (A) and Eu$_2${Pc[(OC$_2$H$_4$)$_3$OCH$_3$]$_8$}[Pc(OCH$_2$CF$_3$)$_8$] (B) in CDCl$_3$. 

S-3
Fig. S3. The molecular dimension of Eu$_2$[Pc(OC$_8$H$_{17}$)$_8$][Pc(OCH$_2$CF$_3$)$_8$](A) : 3.32 nm (length) $\times$ 0.95 nm (height), Eu$_2${Pc[(OC$_2$H$_4$)$_3$OCH$_3$]$_8$}[Pc(OCH$_2$CF$_3$)$_8$](B) : 3.17 nm(length) $\times$ 0.95 nm (height) obtained using PCMODEL for windows Version 6.0, Serena Software.

Fig. S4. Polarized UV-vis spectra of compounds 1-2 (A-B) LS films. 0 and 45° represent the angle between the light and the normal of the substrate, respectively, while “A// and A⊥” represent the absorbance for light polarized with the electric vector parallel and perpendicular to the dipping direction.
**Fig. S5.** XRD pattern recorded in in-plane (grazing incidence) mode for the LS films of 1(A)-2(B).

**Fig. S6.** Current–voltage output plots ($I_{ds}$ vs. $V_{ds}$) of ambipolar OFET device based on LS films of 1(A) and 2(B) deposited on HMDS-treated SiO$_2$/Si (300 nm) substrate with Au top contacts with various $V_G$ for $p$-channel (left column of A and B) measured in air and for $n$-channel (right column of A and B) measured in N$_2$, respectively.
Fig. S7. The recovery time for 1-2 films exposed to NO$_2$ at varied concentration in the range of 0.1-0.85 ppm (exposure: 2 min).

Fig. S8. The time-dependent current evolution curves of the three toxic gases (H$_2$S of 5 ppm, NH$_3$ of 5 ppm, and NO$_2$ of 0.5 ppm) in a sequential testing for LS films of 1(A) and 2(B), the color columns represent exposure time.
**Fig. S9.** The response of the devices for compound 1(A)-2(B) under 0.45 ppm NO₂ exposure of 2 min and 10 min.

**Table S1.** The orientation angle of the phthalocyanine ring determined from polarized UV-vis absorbance of the LS films of compounds 1-2.

<table>
<thead>
<tr>
<th>Compound</th>
<th>A// A⊥</th>
<th>D 0° (A//A⊥)</th>
<th>A// A⊥</th>
<th>D 45° (A//A⊥)</th>
<th>θ°</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.156</td>
<td>0.162</td>
<td>0.96</td>
<td>0.150</td>
<td>0.179</td>
</tr>
<tr>
<td>2</td>
<td>0.145</td>
<td>0.127</td>
<td>1.14</td>
<td>0.106</td>
<td>0.131</td>
</tr>
</tbody>
</table>

**Table S2.** The gate-induced sheet carrier densities \((n)\) of the LS films of compounds 1-2.

<table>
<thead>
<tr>
<th>Cpd</th>
<th>(n_e/\text{cm}^2 (0\text{ V}))</th>
<th>(n_h/\text{cm}^2 (0\text{ V}))</th>
<th>(n_e/\text{cm}^2 (40\text{ V}))</th>
<th>(n_h/\text{cm}^2 (40\text{ V}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(2.48 \times 10^{12})</td>
<td>(8.31 \times 10^9)</td>
<td>(7.68 \times 10^{13})</td>
<td>(1.03 \times 10^{12})</td>
</tr>
<tr>
<td>2</td>
<td>(1.77 \times 10^{12})</td>
<td>(8.01 \times 10^{10})</td>
<td>(4.52 \times 10^{12})</td>
<td>(3.90 \times 10^{12})</td>
</tr>
</tbody>
</table>

\(^a\) Calculated from \(n = (I_{ds}/V_{ds})(L/W)(1/\mu e)\), where \(I_{ds}\) is the source–drain current, \(V_{ds}\) the source–drain voltage, \(W\) the channel width (28.6 mm), \(L\) the channel length (0.24 mm), \(\mu\) the carrier mobility.

In the present system, the carrier densities were calculated at \(V_G=0\text{ V}\) and 40 V, respectively. The values of \((I_{ds}/V_{ds})\) is the slope values of linear region of output characterics when \(V_G=0\text{ V}\) and 40 V, respectively. As seen in Table S2, both \(n_e\) and \(n_h\) at 40 V are higher than \(n_e\) and \(n_h\) at 0 V, which means the gate voltage is an important influence factor of carrier densities. However, no matter 0 V or 40 V,
the $n_e$ of 2 is always smaller than $n_e$ of 1, the $n_h$ of 1 is always smaller than $n_h$ of 2. Note that in the main text, only the carrier densities at $V_G=0$ V were listed in Table 2, representing an original status before gases inject.