Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Fluorination induced electronic effects on Pt(II) square-planar complex of *o*-phenylenediimine ligand.

Luca Pilia, Michio M. Matsushita, Kunio Awaga and Neil Robertson

Supplementary Material

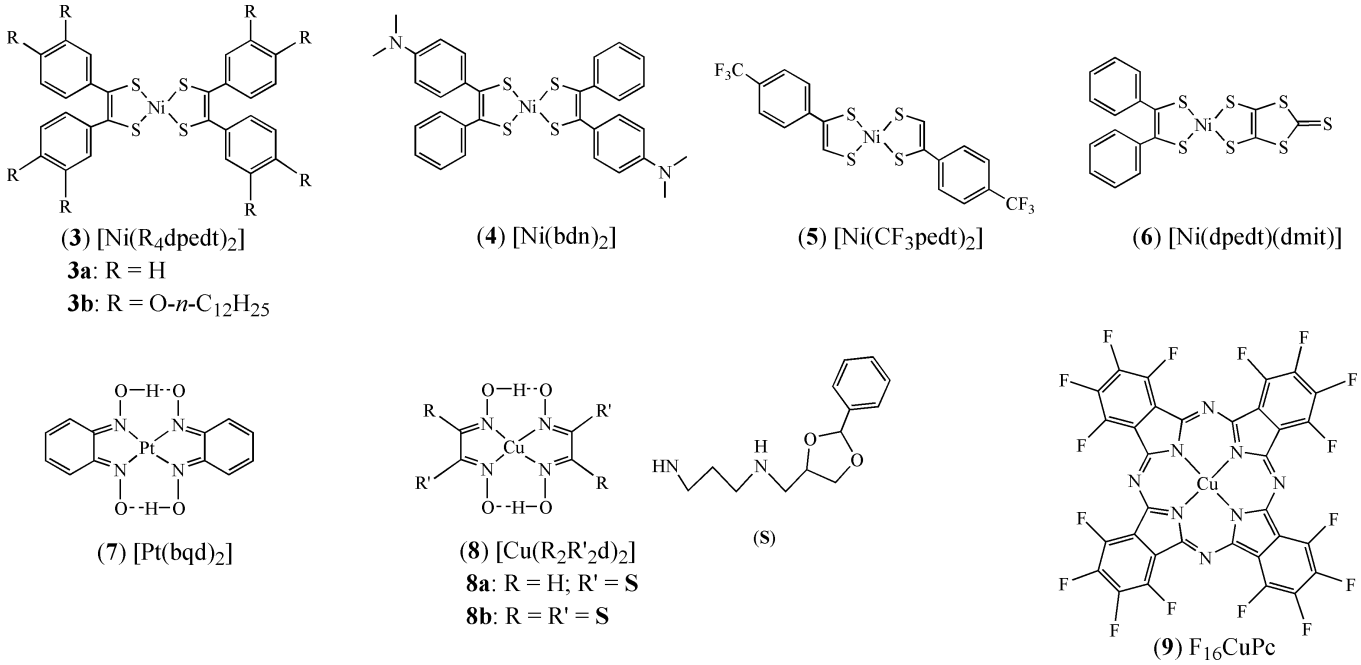


Chart S1 Structural formulae of some *n*-type or ambipolar square-planar metal complexes, whose FET properties are reported in Table S1.

Table S1. FET properties of some *n*-type or ambipolar square-planar metal complexes.

Complex	*p*-type mobility ($cm^2 V^{-1} s^{-1}$)	*n*-type mobility ($cm^2 V^{-1} s^{-1}$)	on/off current ratio	References
$[Ni(dpedt)_2]$ (**3a**)		$2\cdot10^{-5}$	10^2	1
$[Ni(R_4dpedt)_2]$ (**3b**)		$1.3\cdot10^{-3}$	$>10^5$	2
$[Ni(bdn)_2]$ (**4**)	10^{-}	10^{-4}	10^2–10^3	3
$[Ni(CF_3pedt)_2]$ (**5**)		$1.1\cdot10^{-1}$	$2\cdot10^6$	4
$[Ni(H_2dpedt)(dmit)]$ (**6**)	10^{-}	$3\cdot10^{-4}$	10^2–10^3	5
$[Pt(bqd)_2]$ (**7**)		$2\cdot10^{-1}$	1.6	6
$[Cu(HR'd)_2]$ (**8a**)		$2.91\cdot10^{-4}$	*a*	7
$[Cu(R'_2d)_2]$ (**8b**)		$1.52\cdot10^{-3}$	*a*	7
$F_{16}CuPc$ (**9**)		$3\cdot10^{-3}$	*a*	8

a Not available

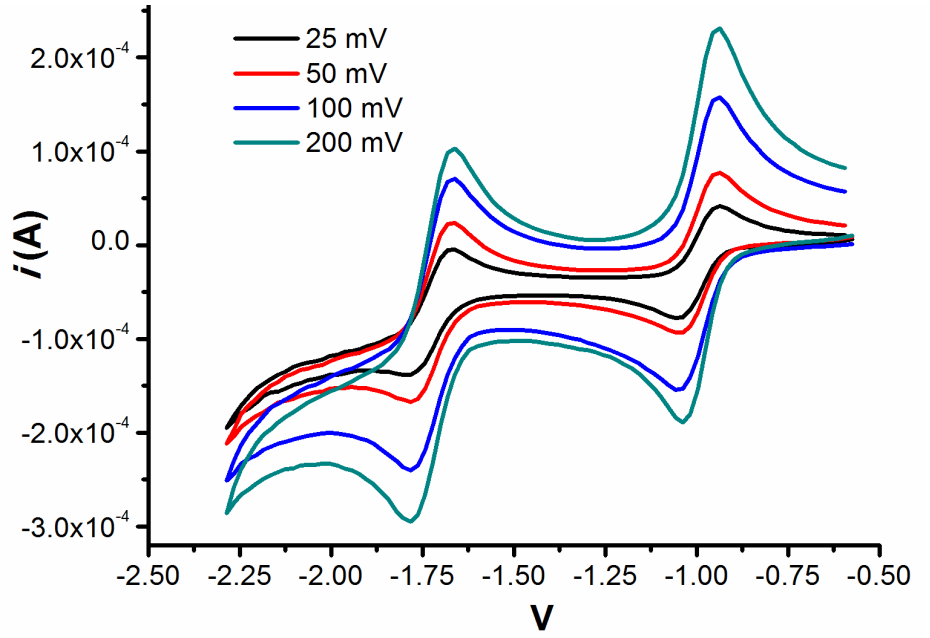


Figure S1. Cyclic voltammograms of **2** recorded at 298 K at different scan rates in a DMF degassed solution, containing 0.1 M Bu_4NPF_6 as supporting electrolyte (V *vs* F_c/F_c^+).

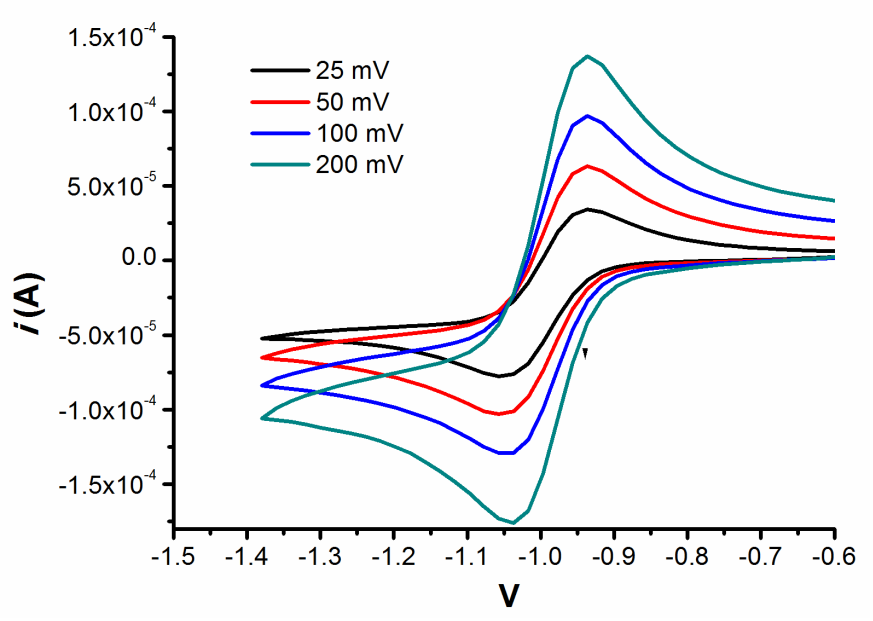


Figure S2. Cyclic voltammograms of **2** recorded at 298 K at different scan rates in a DMF degassed solution, containing 0.1 M Bu_4NPF_6 as supporting electrolyte (V *vs* F_c/F_c^+).

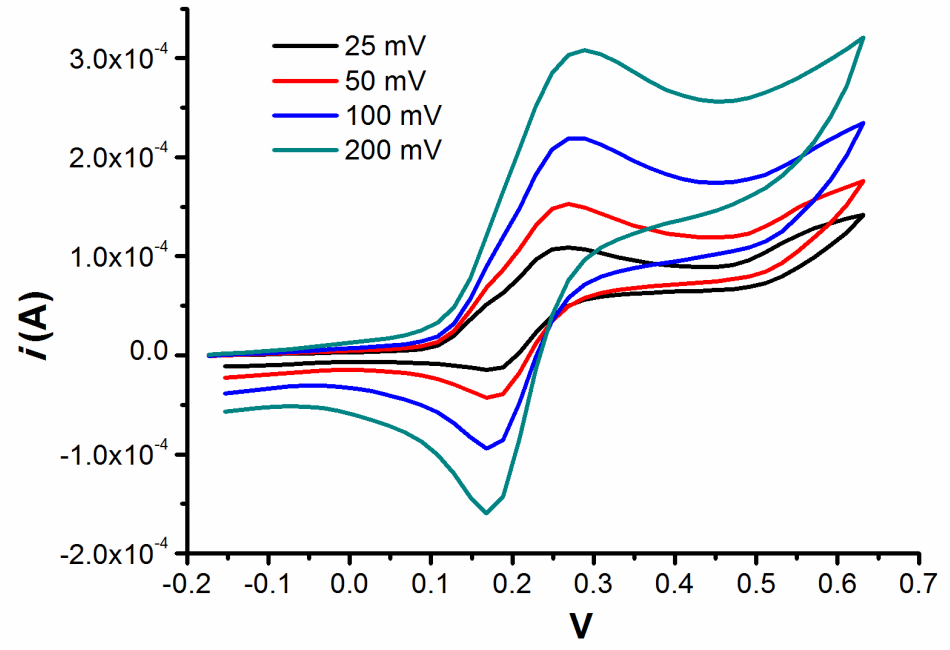


Figure S3. Cyclic voltammograms of **2** recorded at 298 K at different scan rates in a DMF degassed solution, containing 0.1 M Bu_4NPF_6 as supporting electrolyte (V *vs* F_c/F_c^+).

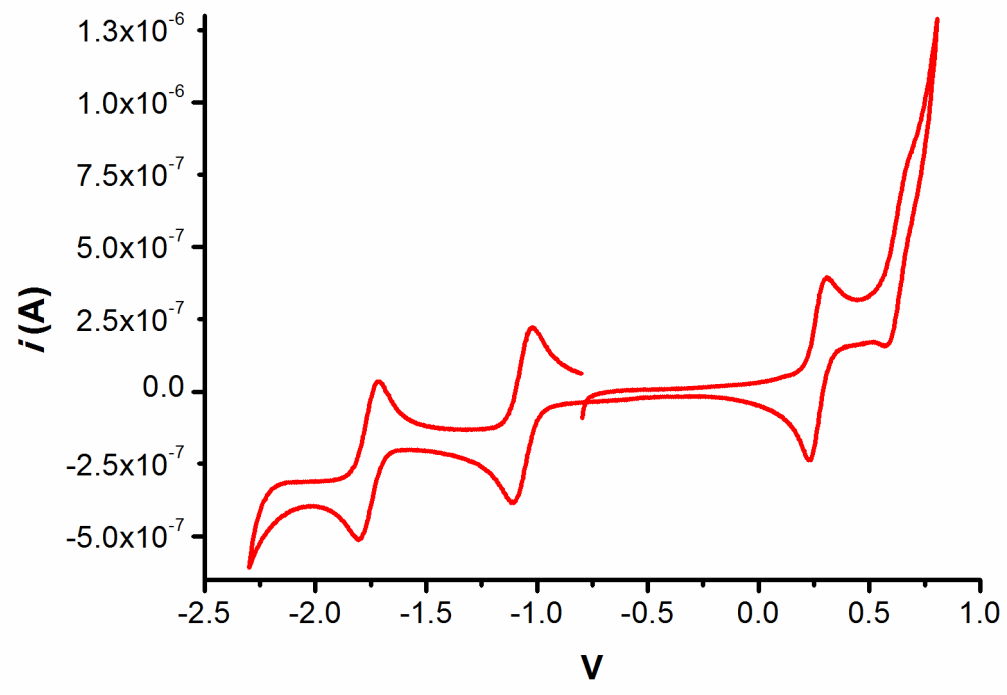


Figure S4. Cyclic voltammetry of **2** measured at the Pt electrode in a THF degassed solution containing 0.1 mol·dm^{-3} Bu_4NPF_6 as supporting electrolyte (V *vs* F_c/F_c^+).

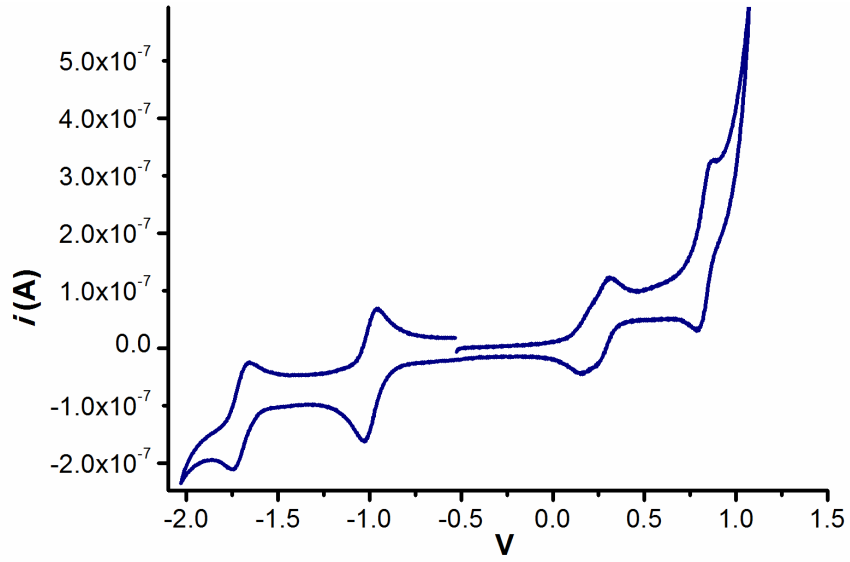


Figure S5. Cyclic voltammetry of **2** measured at the Pt electrode in a CH_2Cl_2 degassed solution containing 0.1 mol·dm^{-3} Bu_4NPF_6 as supporting electrolyte (V *vs* F_c/F_c^+).

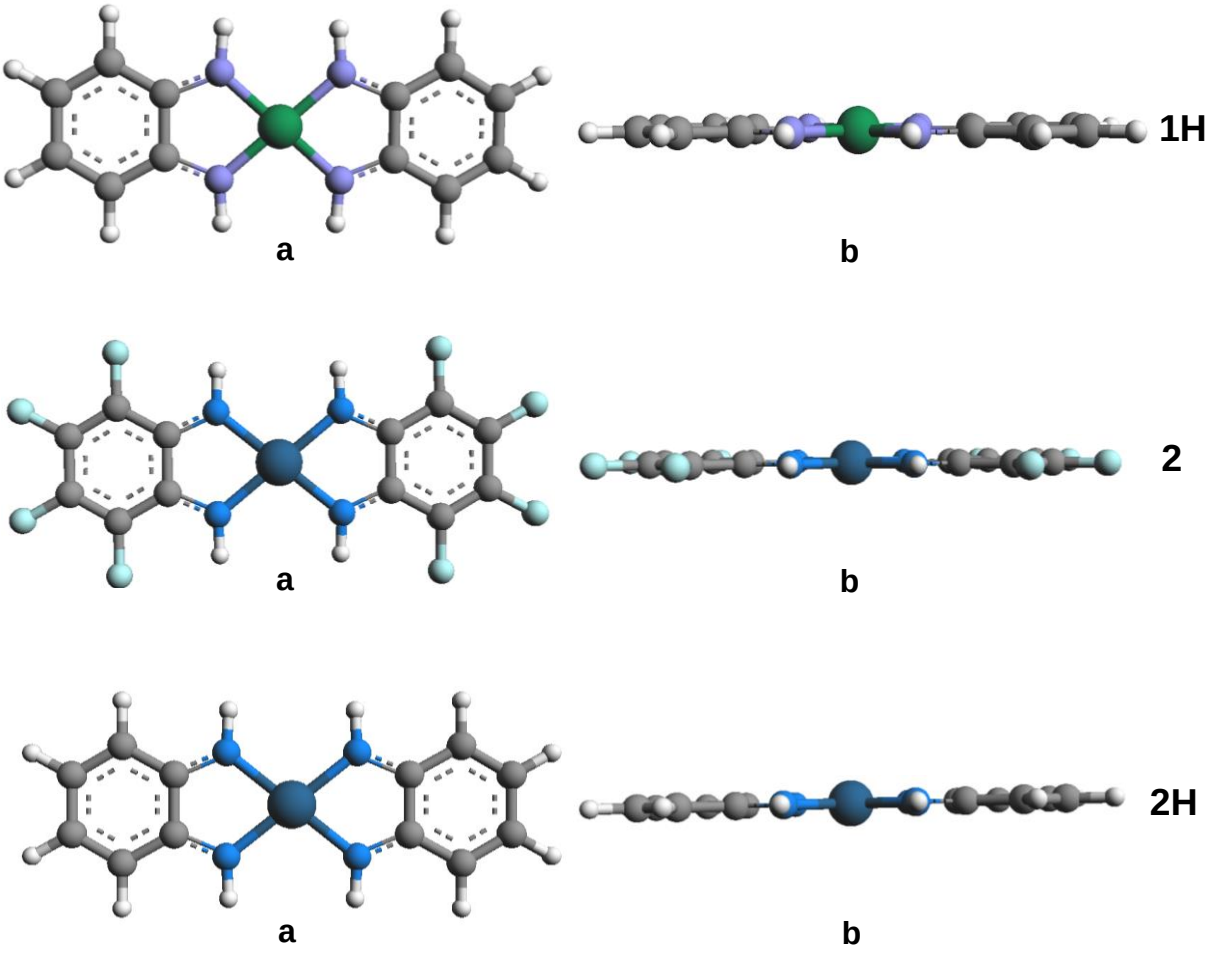


Figure S6. Gas phase optimized geometries of **1H**, **2** and **2H**.

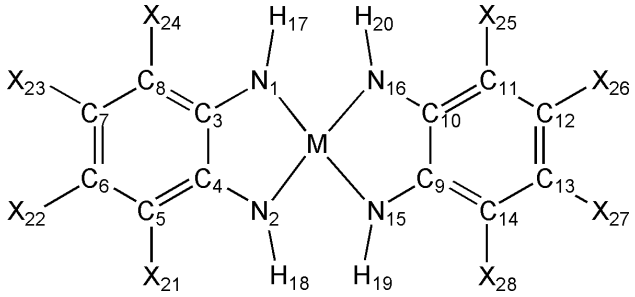


Chart 2S. Structural formula of **1H** (M = Ni, X = H), **2** (M = Pt, X = F) and **2H** (M = Pt, X = H) with atom labels.

Table S2. Comparison of calculated atomic contributions to HOMO and LUMO orbitals of complexes **2** and **2H** in gas-phase. [a]

	2 (X = F)		**2H** (X = H)	
Atoms	**HOMO** (%)	**LUMO** (%)	**HOMO** (%)	**LUMO** (%)
N1, N2, N15, N16	36	42	39	44
C3, C4, C9, C10	29	9	31	8
C5, C8, C11, C14	4	9	7	11
C6, C7, C12, C13	21	11	21	12
X21, X24, X25, X28	1	1	0	0
X22, X23, X26, X27	6	2	0	0
Pt	3	25	2	25
H17, H18, H19, H20	0	1	0	0

[a] Calculated by DFT calculations at B3LYP/6-311+G(d,p) level of theory.

Table S3. Comparison of calculated atomic percentage contributions to HOMO and LUMO orbitals of complexes **1H**, **2** and **2H** in CH_2Cl_2. [a]

	1H (M = Ni; X = H;)		**2** (M = Pt, X = F)		**2H** (M = Pt, X = H)	
Atoms	**HOMO**	**LUMO**	**HOMO**	**LUMO**	**HOMO**	**LUMO**
N_1, N_2, N_{15}, N_{16}	38	46	37	42	38	43
C_3, C_4, C_9, C_{10}	31	12	28	8	31	9
C_5, C_8, C_{11}, C_{14}	8	13	5	10	6	11
C_6, C_7, C_{12}, C_{13}	22	15	20	11	21	12
X_{21}, X_{24}, X_{25}, X_{28}	0	0	1	1	0	0
X_{22}, X_{23}, X_{26}, X_{27}	0	0	5	2	0	0
M	2	12	3	25	4	25
H_{17}, H_{18}, H_{19}, H_{20}	0	0	1	1	0	0

[a] Calculated by DFT calculations at B3LYP/6-311+G(d,p) level of theory.

Table S4. Calculated frontier orbitals' energies in the gas phase and CH_2Cl_2 simulated solution for the complexes **2** and **2H**. [a]

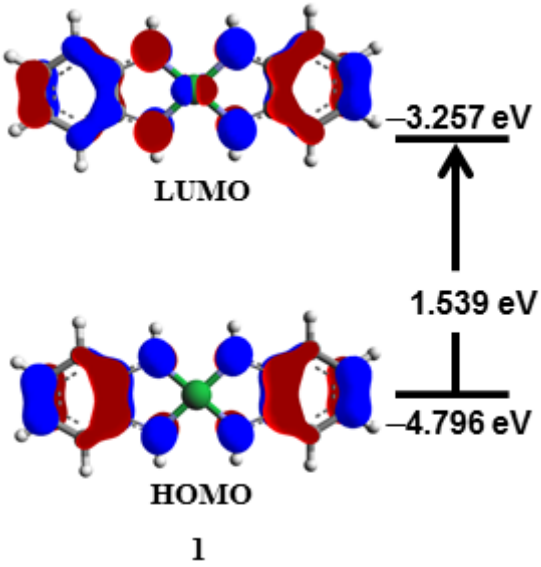
Gas phase	**2**	**2H**
LUMO+4	–0.763	–0.116
LUMO+3	–0.983	–0.180
LUMO+2	–1.208	–0.308
LUMO+1	–1.249	–0.355
LUMO	**–4.105**	**–3.130**
HOMO	**–5.872**	**–4.893**
HOMO–1	–6.537	–5.651
HOMO–2	–7.077	–6.350
HOMO–3	–7.843	–6.901
HOMO–4	–8.077	–7.187
CH_2Cl_2	**2**	**2H**
LUMO+4	–0.528	–0,159
LUMO+3	–0.868	–0,167
LUMO+2	–0.879	–0,256
LUMO+1	–1.038	–0,417
LUMO	**–3.804**	**–3,239**
HOMO	**–5.602**	**–5,022**
HOMO–1	–6.257	–5,759
HOMO–2	–6.848	–6,458
HOMO–3	–7.425	–7,011
HOMO–4	–7.814	–7,312

[a] Calculated by DFT calculations at B3LYP/6-311+G(d,p) level of theory.

Table S5. HOMO-LUMO gaps for complexes **1H**, **2H** and **2**.

	1H	**2H**	**2**
Exp. [a]	1.01 eV	1.15 eV	1.21 eV
Gas phase [b]	1.54 eV	1.76 eV	1.77 eV
CH_2Cl_2 [b]	1.56 eV	1.78 eV	1.80 eV

[a] Estimated from electrochemical data; [b] calculated by DFT calculations at B3LYP/6-311+G(d,p) level of theory.



1

Figure S7. FOs of **1H** calculated by DFT methods at B3LYP/6-311+G(d,p) level of theory and plotted with a contour value of 0.040.

Table S6. Calculated frontier orbitals' energies in the gas phase for complex **1H**.[a]

	Gas phase	**CH_2Cl_2**
LUMO+4	0.005	–0.105
LUMO+3	–0.232	–0.278
LUMO+2	–0.320	–0.350
LUMO+1	–1.202	–1.298
LUMO	**–3.257**	**–3.379**
HOMO	**–4.796**	**–4.940**
HOMO–1	–5.870	–5.993
HOMO–2	–6.220	–6.339
HOMO–3	–6.839	–6.989
HOMO–4	–7.111	–7.250

[a] Calculated by DFT calculations at B3LYP/6-311+G(d,p) level of theory.

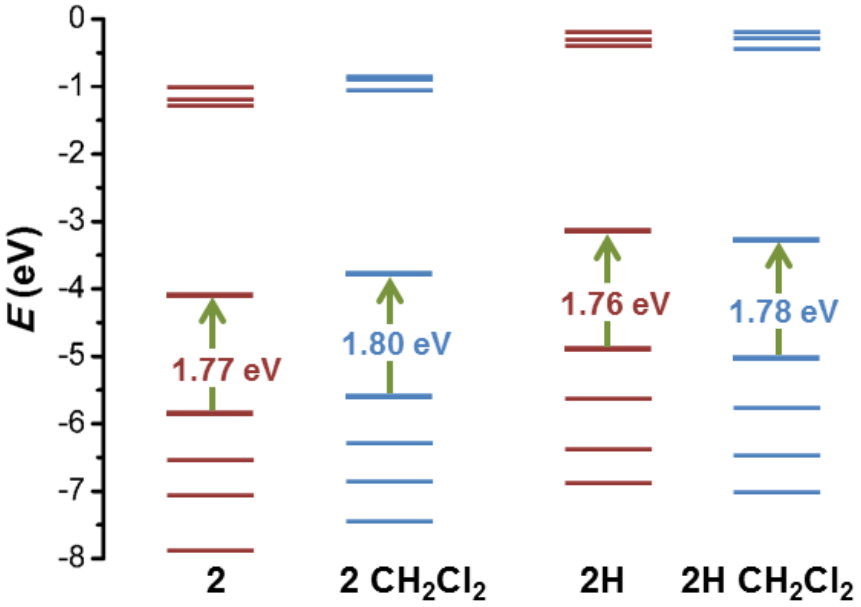


Figure S8. Energy levels diagram for **2** and **2H** complexes, calculated in gas phase and CH_2Cl_2 at B3LYP/6-311+G(d,p) level of theory

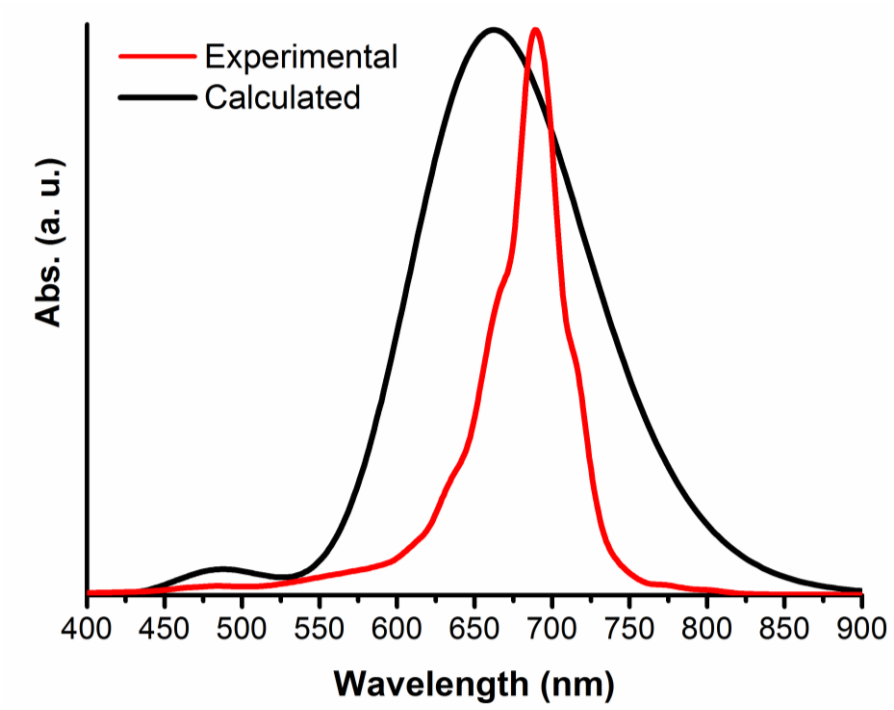


Figure S9. Comparison between the experimental and calculated electronic spectra of **2**, which were measured in CH_2Cl_2 solution and calculated by TD-DFT methods in the same solvent, respectively.

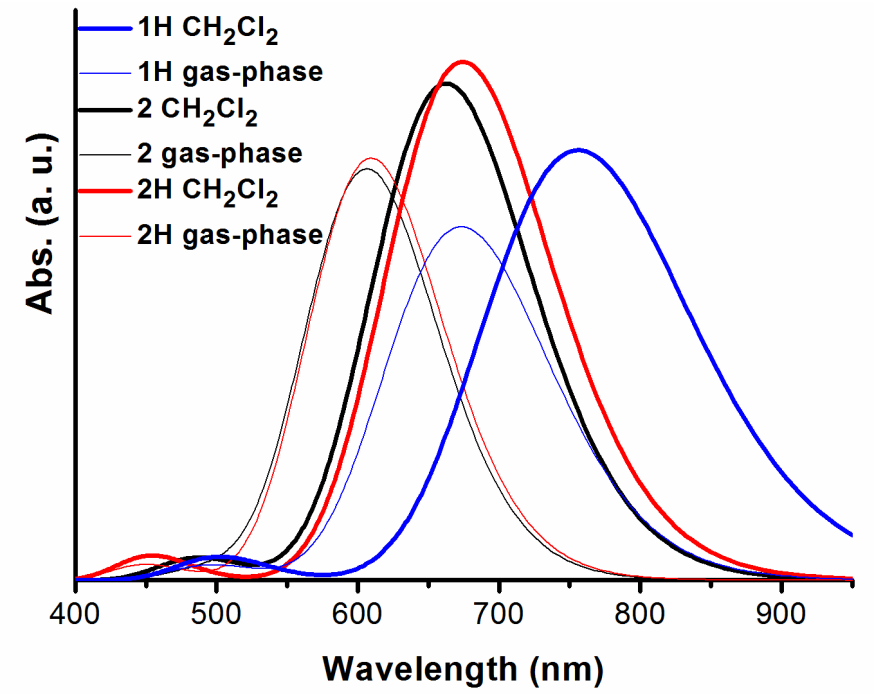


Figure S10. Comparison between the TD-DFT calculated electronic spectra of **1H**, **2** and **2H**, in both gas phase and in CH_2Cl_2.

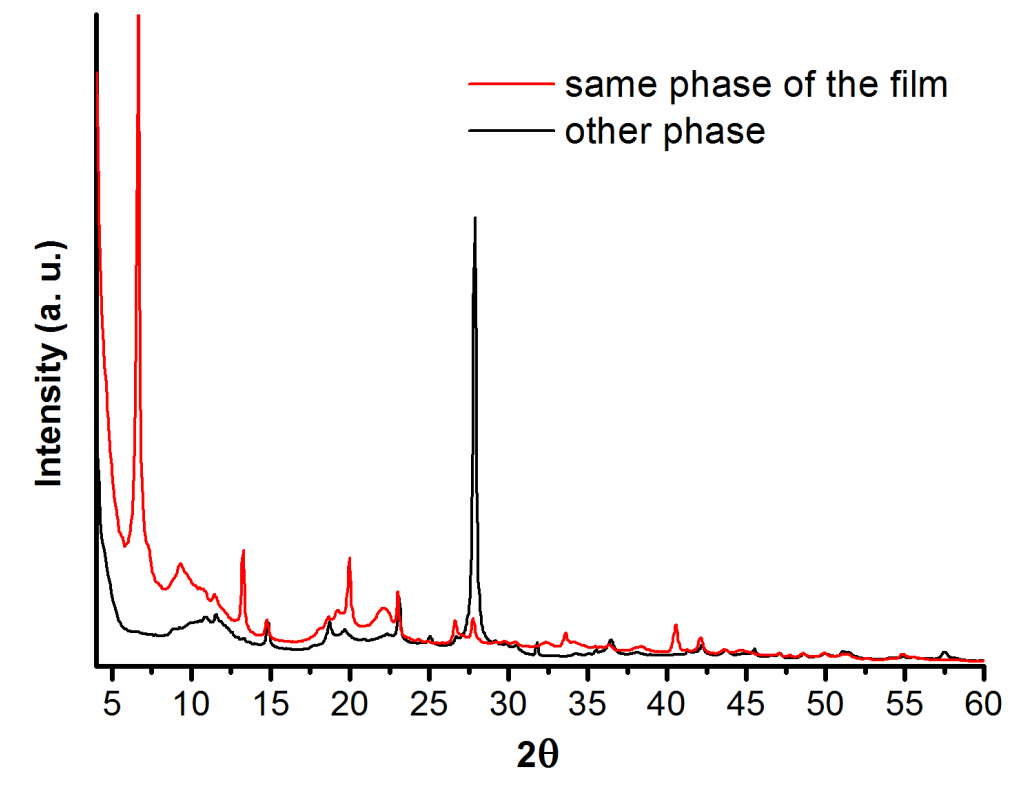


Figure S11. Comparison between the XRD patterns of two different samples of **2**.

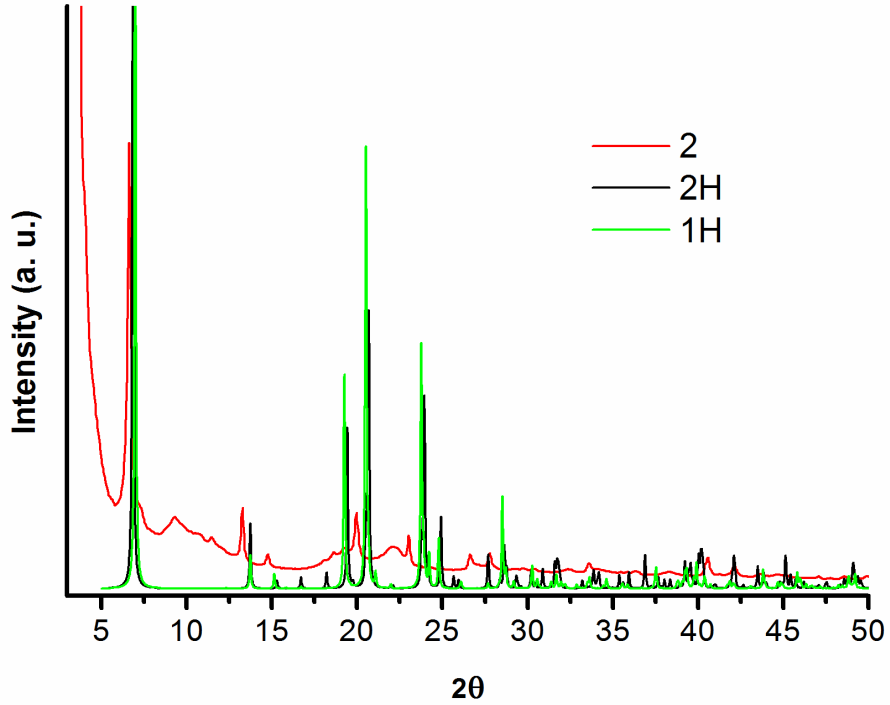


Figure S12. Comparison between the XRD patterns of **1H** and **2H** simulated from single crystal data and the experimental one of **2**.

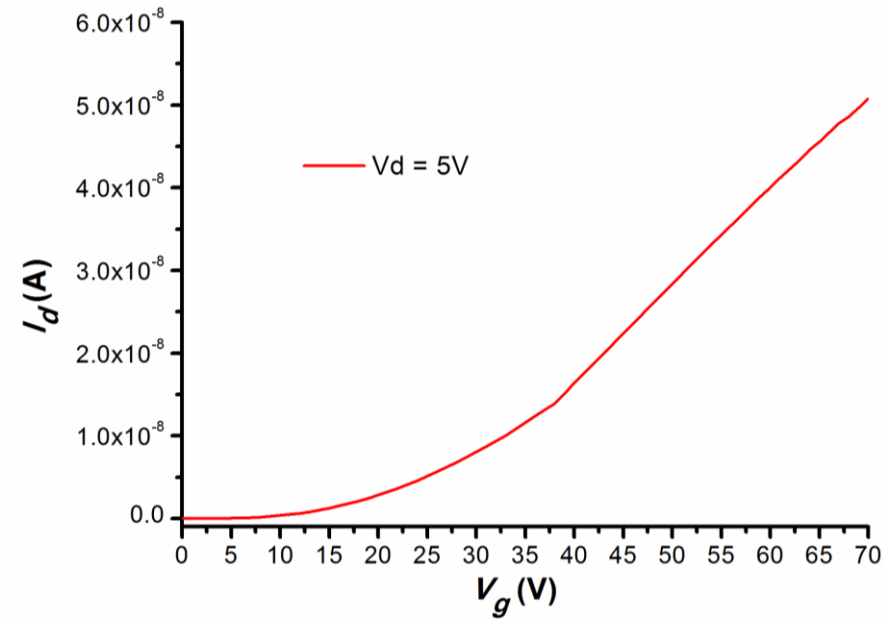


Figure S13. Transfer characteristics of **2** measured on 2 x 2 μm substrates.

References

1. T. Taguchi, H. Wada, T. Kambayashi, B. Noda, M. Goto, T. Mori, K. Ishikawa and H. Takezoe, *Phys. Chem. Lett.*, **421**, 395 (2006).
2. J.-Y. Cho, B. Domercq, S. C. Jones, J. Yu, X. Zhang, Z. An, M. Bishop, S. Barlow, S. R. Marder and B. Kippelen, *J. Mater. Chem.*, **17**, 2642 (2007).
3. T. D. Anthopoulos, S. Setayesh, E. Smits, M. Cölle, E. Cantatore, B. de Boer, P. W. M. Blom and D. M. de Leeuw, *Adv. Mater.*, **18**, 1900 (2006).
4. L. Qu, Y. Guo, H. Luo, C. Zhong, G. Yu, Y. Liu and J. Qin, *Chem. Commun.*, 48, 9965 (2012).
5. T. D. Anthopoulos, G. C. Anyfantis, G. C. Papavassiliou, and D. M. de Leeuw, *Appl. Phys. Lett.*, **90**, 122105 (2007).
6. K.-I. Sakai, T. Hasegawa, M. Ichikawa, Y. Taniguchi, *Chem. Lett.*, 35, 302 (2006).
7. Y. Aydogdu, F. Yakuphanoglu, A. Aydogdu, E. Tas, A. Cukurovali, *Mater. Lett.* 57 (2003) 3755–3760
8. Z. Bao, A. J. Lovinger, J. Brown, *J. Am. Chem. Soc.*, 120, 207 (1998).