## **Supporting Information**

### [FeFe]-Hydrogenase H-Cluster Mimics Mediated by Naphthalene Monoimide Derivatives of *Peri*-Substituted Dichalcogenides

Hassan Abul-Futouh,<sup>a†</sup> Yulian Zagranyarski,<sup>b†</sup> Carolin Müller,<sup>c</sup> Martin Schulz,<sup>c</sup> Stephan Kupfer,<sup>c</sup> Helmar Görls,<sup>a</sup> Mohammad El-khateeb,<sup>d</sup> Stefanie Gräfe,<sup>c</sup> Benjamin Dietzek,<sup>c,e</sup> Kalina Peneva,<sup>f,g\*</sup> and Wolfgang Weigand<sup>a\*</sup>

<sup>a</sup> Institut für Anorganische und Analytische Chemie, Friedrich-Schiller-Universität Jena, Humboldt Str. 8, 07743 Jena, Germany. Email: wolfgang.weigand@uni-jena.de.

<sup>b</sup> Faculty of Chemistry and Pharmacy, Sofia University 'St. Kliment Ohridski', 1 James Bourchier Ave., Sofia 1164, Bulgaria.

<sup>c</sup> Institut für Physikalische Chemie and Abbe Center of Photonics, Friedrich-Schiller-Universität Jena, Helmholtzweg 4, 07743 Jena, Germany.

<sup>d</sup> Chemistry Department, Jordan University of Science and Technology, Irbid 22110, Jordan.

<sup>e</sup> Leibniz-Institut für Photonische Technologien e.V., Department of Functional Interfaces, Albert-Einstein-Str. 9, 07745 Jena, Germany.

<sup>f</sup> Institute of Organic Chemistry and Macromolecular Chemistry, Friedrich-Schiller-University Jena, Lessingstrasse 8, 07743 Jena, Germany, Email: kalina.peneva@uni-jena.de.

<sup>g</sup> Center for Energy and Environmental Chemistry Jena (CEEC Jena), Friedrich-Schiller-University, Philosophenweg 7a, 07743 Jena, Germany.

 ${\ensuremath{{/}}}$  These authors contributed equally

#### General experimental details

A ll solvents and starting materials that have not been synthesized by us were commercial products (Acros Organics, Fisher Scientific, Fluka, Merck and Sigma Aldrich,) and were used without further purification. The progress of all reactions was monitored by thin layer chromatography (Macherey- Nagel F 254 silica gel sheet) with appropriate solvents described for each compound in the synthetic procedures. Column chromatography purifications were carried out on silica gel from Macherey Nagel (0.063 mm – 0.200 mm). NMR spectra were recorded on Bruker Avance 500MHz instruments. Spectra (<sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}) were referenced to appropoate residual solvent signals (CDCl<sub>3</sub>, DMSO-d<sup>6</sup>) and Se{<sup>1</sup>H}-NMR to Me<sub>2</sub>Se. Elemental analysis was performed with a Leco CHNS-932 apparatus.

#### Procedures for the preparation of the precursors B-E.





To a solution of 1,8-naphthalic anhydride (50 mmol, 9.92 g) in 500 ml sulfuric acid (95-97%) at room temperature, NBS (300 mmol, 53.40 g) was added. The reaction mixture was stirred at room temperature for 24 h and the mixture was poured into 500 g ice. The precipitate was filtered and washed several times with water and dried. Yield of crude product 24.0 g (93%). The crude product was recrystallized from chlorobenzene to give compound **B** as a white solid. Yield 21.30 g (83%). Elemental analysis for  $C_{12}H_2Br_4O_3$ : calculated C 28.05, H 0.39; found C 27.91, H 0.28. <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sup>6</sup>, ppm):  $\delta$  = 8.69, (s, 2H). <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, DMSO-*d*<sup>6</sup>, ppm):  $\delta$  = 158.8, 135.5, 132.0, 130.7, 129.6, 129.5, 120.7.





To a solution of 1,8-naphthalic anhydride (40 mmol, 7.93 g) in sulfuric acid (95-97%, 150 ml) at room temperature, TCCA (60 mmol, 13.95 g) was added. The reaction mixture was heated at 90°C for 30 min and then slowly increases to 110°C and stirred for 1 h. The mixture was cooled to room temperature and poured into 300 g ice. The precipitate was filtered and washed several times with water and dried. The crude product was recrystallized from chlorobenzene to give compound **C** as a white solid. Yield 12.20 g (91%). Elemental analysis for  $C_{12}H_2Cl_4O_3$ : calculated C 42.90, H 0.60; found C 43.11, H 0.55. <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sup>6</sup>, ppm):  $\delta$  = 8.67, (s, 2H). <sup>13</sup>C {<sup>1</sup>H} NMR (125 MHz, DMSO-*d*<sup>6</sup>, ppm):  $\delta$  = 158.6, 136.1, 134.4, 133.0, 129.7, 128.0, 120.3.

# Synthesisof5,6,7,8-tetrabromo-2-(2,6-diisopropylphenyl)-1H-benzo[de]isoquinoline-1,3(2H)-dione (D).



A mixture of 3,4,5,6-tetrabromonaphthalene monoanhydride (**B**) (10.0 mmol, 5.14 g), 2,6-diisopropylaniline (20.0 mmol, 3.54 g) in NMP (30 ml ) and acetic acid (30 ml) was stirred at 150°C for 2 h. The reaction mixture was poured into ice (100 g) and the precipitate was filtered and dried. The crude product was purified by column chromatography (SiO<sub>2</sub>, hexane-dichloromethane, 3:2) to give the diimide **D** as a white solid. Yield 5.45 g (81%). Elemental analysis for C<sub>24</sub>H<sub>19</sub>Br<sub>4</sub>NO<sub>2</sub>: calculated C 42.83, H 2.85, N 2.08; found C 42.60, H 2.71, N 1.87. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  =

8.86 (s, 2H), 7.50 (t, J = 7.8 Hz, 1H), 7.33 (d, J = 7.8 Hz, 2H), 2.62 (hept, J = 6.7 Hz, 2H), 1.15 (d, J = 6.9 Hz, 12H). <sup>13</sup>C{H} NMR (125 MHz, CDCl<sub>3</sub>, ppm):  $\delta = 162.2$ , 145.6, 136.2, 133.1, 131.6, 130.2, 130.2, 129.8, 128.5, 124.4, 122.9, 29.4, 24.1. Synthesis of 5,6,7,8-tetrachloro-2-(2,6-diisopropylphenyl)-1*H*-

benzo[*de*]isoquinoline-1,3(2*H*)-dione (E).



A mixture of 3,4,5,6-tetrachloronaphthalene monoanhydride (**C**) (20.0 mmol, 6.72 g), 2,6-diisopropylaniline (40.0 mmol, 7.08 g) in NMP (30 ml) and acetic acid (30 ml) was stirred at 140°C for 2 h. The reaction mixture was poured into ice (100 g) and the precipitate was filtered and dried. The crude product was purified by column chromatography (SiO<sub>2</sub>, hexane-dichloromethane, 3:2) to give the diimide **E** as a white solid. Yield 8.69 g (88%). Elemental analysis for C<sub>24</sub>H<sub>19</sub>Cl<sub>4</sub>NO<sub>2</sub>: calculated C 58.21, H 3.87, N 2.83; found C 57.99, H 3.73, N 2.93. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  = 8.74 (s, 2H), 7.50 (t, *J* = 7.8 Hz, 1H), 7.33 (d, *J* = 7.8 Hz, 2H), 2.63 (hept, *J* = 6.8 Hz, 2H), 1.15 (d, *J* = 6.9 Hz, 12H). <sup>13</sup>C{H} NMR (125 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  = 162.1, 145.6, 137.3, 135.9, 133.4, 130.2, 129.8, 129.3, 128.4, 124.4, 122.4, 29.4, 24.1.

**Figure S1.** Molecular structure (60% probability) of compound **6**. Two crystallographically independent molecules and one molecules of dichloromethane were determined in the unit cell of compound **6**, only one of them is shown here. The hydrogen atoms are omitted for clarity reasons.



**Figure S2.** Motif structure of complex 7. Due to the poor quality of the crystal we could not deposit this complex in the Cambridge data base.



Figure S3. (Top): Cyclic voltammetry of (a) 1.0 mM complex 7 and (b) 1.0 mM complex 8 in  $CH_2Cl_2$ -[*n*-Bu<sub>4</sub>N][BF<sub>4</sub>] (0.1 M) solutions at various scan rates. (Bottom): The reverse scan at 0.2 V s<sup>-1</sup> of the first reduction peaks of (a) complex 7 and (b) complex 8. The arrows indicate the scan direction. The potentials *E* are given in V and referenced to the Fc<sup>+</sup>/Fc couple.



**Figure S4.** Plot of the cathodic current function *vs* scan rates for the first and second reduction waves of complexes **7** and **8**.



**Figure S5.** Plot of the cathodic current function *vs* scan rates for the first and second reduction waves of complexes **9** and **10**.



**Figure S6**. Cyclic voltammetry of 1.0 mM complex **9** in  $CH_2Cl_2$ -[*n*-Bu<sub>4</sub>N][BF<sub>4</sub>] (0.1 M) solutions at (**a**) 0.2 V s<sup>-1</sup> scan rate, the red and the blue profiles show the reverse scan of the first and the second reduction peaks of complex **9**. (**b**) Various scan rates of complexes **9**. The arrows indicate the scan direction. The potentials *E* are given in V and referenced to the Fc<sup>+</sup>/Fc couple.



**Figure S7**. Cyclic voltammetry of 1.0 mM complex **10** in  $CH_2Cl_2$ -[*n*-Bu<sub>4</sub>N][BF<sub>4</sub>] (0.1 M) solutions at (**a**) 0.2 V s<sup>-1</sup> scan rate, the red profile shows the reverse scan of the first reduction peak of complex **10**. (**b**) Various scan rates of complexes **10**. The arrows indicate the scan direction. The potentials *E* are given in V and referenced to the Fc<sup>+</sup>/Fc couple.



**Figure S8.** Repeated scan of complexes 7-10 in  $CH_2Cl_2$ -[*n*-Bu<sub>4</sub>N][BF<sub>4</sub>] (0.1 M) solutions at 0.2 V s<sup>-1</sup> scan rate. The arrows indicate the scan direction. The potentials *E* are given in V and referenced to the Fc<sup>+</sup>/Fc couple.



**Figure S9.** Cyclic voltammogam of various concentration of AcOH in  $CH_2Cl_2$ -[*n*-Bu<sub>4</sub>N][BF<sub>4</sub>] (0.1 M) solution at 0.2 V s<sup>-1</sup> scan rate in the absence of complexes **7-10**. The arrows indicate the scan direction. The potentials *E* are given in V and referenced to the Fc<sup>+</sup>/Fc couple.



**Figure S10.** Contour plot of the emission characteristics of compound **1** (left) and compound **2** (right) obtained in dichloromethane. Horizontal reading gives the emission spectra at the respective excitation wavelength. Vertical reading gives the excitation spectra at the respective emission wavelength. Diagonal signals are due to residues of the excitation light and second order stray light as well as the solvent Raman band.



**Figure S11.** Contour plot of the emission characteristics of compound **4** (left) and compound **5** (right) obtained in dichloromethane. Horizontal reading gives the emission spectra at the respective excitation wavelength. Vertical reading gives the excitation spectra at the respective emission wavelength. Diagonal signals are due to residues of the excitation light and second order stray light as well as the solvent Raman band.



**Figure S12.** Contour plot of the emission characteristics of compound 7 (left) and compound 8 (right) obtained in dichloromethane. Horizontal reading gives the emission spectra at the respective excitation wavelength. Vertical reading gives the excitation spectra at the respective emission wavelength. Diagonal signals are due to residues of the excitation light and second order stray light as well as the solvent Raman band.



**Figure S13.** Contour plot of the emission characteristics of compound **9** (left) and compound **10** (right) obtained in dichloromethane. Horizontal reading gives the emission spectra at the respective excitation wavelength. Vertical reading gives the excitation spectra at the respective emission wavelength. Diagonal signals are due to residues of the excitation light and second order stray light as well as the solvent Raman band.



**Table S1:** Structural parameters such as selected bond lengths (d/pm), bond angles ( $\alpha/\circ$ ) and dihedral angles ( $\delta/\circ$ ) for the equilibrium geometries of complexes 7 and 9 at the BP86/TZVP level of theory (in dichloromethane) and the X-ray structure of complex 9.

		$7(X_1 = X_2 = S)$	<b>9</b> ( $X_1 = X_2 = Se$ )	
		BP86	X-ray	BP86
	$d(\mathrm{Fe}_1,\mathrm{X}_1) / \mathrm{pm}$	229.0	235.6(7)	239.8
	$d(\mathrm{Fe}_1,\mathrm{X}_2) / \mathrm{pm}$	229.0	236.5(7)	239.8
R	$d(\mathrm{Fe}_2,\mathrm{X}_1) / \mathrm{pm}$	229.0	236.2(7)	239.7
	$d(\mathrm{Fe}_2, \mathrm{X}_2) / \mathrm{pm}$	229.0	235.7(6)	239.7
grige .	$\alpha(X_1,C_1,X_2) / \circ$	64.50	64.56	64.56
	$\alpha$ (O <sub>1</sub> ,Fe <sub>1</sub> ,O <sub>2</sub> ) / °	98.32	98.64	98.66
	$\alpha$ (O <sub>1</sub> ,Fe <sub>1</sub> ,O <sub>3</sub> ) / °	98.32	103.79	98.66
	$\alpha$ (O <sub>2</sub> ,Fe <sub>1</sub> ,O <sub>3</sub> ) / °	90.51	91.88	90.42
	$\alpha$ (O <sub>4</sub> ,Fe <sub>2</sub> ,O <sub>5</sub> ) / °	98.28	101.82	98.62
Fel Fe2	$\alpha(O_4,Fe_2,O_6) / \circ$	98.28	97.67	98.62
	$\alpha(O_5,Fe_2,O_6) / \circ$	90.49	86.68	90.46
<b>UB</b> - <b>O</b> 5	$\delta(O_1, Fe_1, C_1, C_2) / \circ$	0.03	4.20	0.03
	$\partial (O_4, Fe_2, C_1, C_2) / \circ$	0.03	12.19	0.03

**Table S2:** Excited state properties, obtained at the TD-B3LYP/TZVP level of theory within dichloromethane using a PCM, of complexes 7 and 9 associated to the main absorption features within the Uv/Vis region, namely, leading transitions with weights (%), excitation energies  $E^e$  (eV), wave lengths  $\lambda$  (nm), oscillator strengths f and assigned experimental absorption bands  $\lambda_{exp}$ .

		7				
State	Transition	weight	E <sup>e</sup> /	λ/	f	$\lambda_{\rm exp}$ /
		%	eV	nm		nm
S <sub>2</sub>	$p_{S}(153) \rightarrow \sigma_{FeFe}*(158) (LMCT)$ $\pi + d_{Fe}(149) \rightarrow \sigma_{FeFe}*(158)$ $(LMCT)$ $\pi + d_{Fe}(147) \rightarrow \sigma_{FeFe}*(158)$ $(LMCT)$	50 21 11	2.89	428	0.012	464
<b>S</b> <sub>3</sub>	$d_{Fe}(148) \rightarrow \sigma_{FeFe}^{*}(158) (MC)$ $p_{S}(153) \rightarrow \pi^{*}(157) (ILCT)$ $\pi(155) \rightarrow \sigma_{FeFe}^{*}(158) (LMCT)$	54 15 10	2.96	419	0.002	464
$S_4$	$\sigma_{\text{FeFe}}(156) \rightarrow \sigma_{\text{FeFe}}^{*}(158) (\text{MC})$ $p_{\text{S}}(154) \rightarrow \pi^{*}(157) (\text{ILCT})$	55 34	3.00	413	0.082	464
$S_7$	$\pi(155) \to \pi^*(157)$ (IL)	96	3.11	398	0.544	375
$S_9$	$p_{S}(154) \rightarrow \pi^{*}(157) (ILCT)$	44	3.24	383	0.138	375
	$\sigma_{\text{FeFe}}(156) \rightarrow \sigma_{\text{FeFe}}^{*}(158) (\text{MC})$	25				
		9				
State	Transition	weight	$E^e$ /	λ/	f	$\lambda_{\rm exp}$ /
		%	eV	nm	U	nm
S <sub>2</sub>	$p_{Se}(171) \rightarrow \sigma_{FeFe}^{*}(176) \text{ (LMCT)}$ $\pi + d_{Fe}(166) \rightarrow \sigma_{FeFe}^{*}(176) \text{ (LMCT)}$	55 20	2.86	434	0.014	471
$S_3$	$\sigma_{\text{FeFe}}(174) \rightarrow \sigma_{\text{FeFe}}^{*}(176) \text{ (MC)}$ $p_{\text{Se}}(172) \rightarrow \pi^{*}(175) \text{ (ILCT)}$	51 39	2.91	426	0.059	471
$S_4$	$n_{O}+d_{Fe}(168) \rightarrow \sigma_{FeFe}*(176)$ (LMCT) $\pi(173) \rightarrow \sigma_{FeFe}*(176)$ (LMCT) $n_{O}+d_{Fe}(167) \rightarrow \sigma_{FeFe}*(176)$ (LMCT) $p_{Se}(171) \rightarrow \pi^{*}(175)$ (LLCT)	42 15 12 10	2.92	423	0.002	471
$S_7$	$\pi(173) \to \pi^*(175)$ (IL)	93	3.13	397	0.519	370
$S_9$	$p_{Se}(172) \rightarrow \pi^*(175) (ILCT)$	47	3.17	391	0.126	370
	$\sigma_{\text{FeFe}}(174) \rightarrow \sigma_{\text{FeFe}}^{*}(176) (\text{MC})$	29				

**Table S3:** Molecular orbitals involved in the leading transitions of the excited stateslisted in Table S2 for complex 7.





**Table S4:** Molecular orbitals involved in the leading transitions of the excited stateslisted in Table S2 for complex 9.

Compound	6	7	8	9
formula	$C_{24}H_{20}Cl_3NO_2Se_2$	$C_{27}H_{24}Fe_2NO_8S_2$	$C_{32}H_{23}Br_2Cl_4Fe_2NO_8S_2[*]$	C <sub>26</sub> H <sub>21</sub> Fe <sub>2</sub> NO <sub>8</sub> Se <sub>2</sub>
fw (g·mol <sup>-1</sup> )	624.68	672.80	1026.95[*]	745.06
T/°Č	-140(2)	-140(2)	-140(2)	-140(2)
crystal system	monoclinic	triclinic	orthorhombic	monoclinic
space group	$P 2_1/n$	Ρī	P 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	$P 2_1/c$
a/ Å	8.2929(2)	9.3219(3)	13.9262(3)	15.9293(5)
b∕ Å	27.6030(6)	18.0889(5)	14.1295(3)	10.8047(3)
<i>c</i> / Å	21.7671(4)	18.3328(6)	19.6116(3)	16.2295(5)
$\alpha/^{\circ}$	90	100.726(2)	90	90
$\beta/^{\circ}$	98.931(1)	93.001(2)	90	95.760(1)
γ/°	90	91.652(2)	90	90
$V/Å^3$	4922.27(18)	3030.81(16)	3858.98(13)	2779.18(14)
Ζ	8	4	4	4
$\rho$ (g·cm <sup>-3</sup> )	1.686	1.474	1.768[*]	1.781
$\mu$ (cm <sup>-1</sup> )	33.53	11.42	32.57[*]	37.12
measured data	33596	13452	23620	17737
data with $I > 2\sigma(I)$	8798	9972	7849	5292
unique data (R <sub>int</sub> )	11117/0.0567	13452/0.0718	8839/0.0599	6275/0.0510
w $R_2$ (all data, on F <sup>2</sup> ) <sup>a)</sup>	0.1017	0.3845	0.1156	0.0879
$R_1 (I > 2\sigma(I))^{a}$	0.0481	0.1475	0.0523	0.0408
S <sup>b)</sup>	1.067	1.112	1.092	1.065
Res. dens./e·Å <sup>-3</sup>	1.129/-0.515	1.788/-1.455	1.422/-0.943	0.580/-0.603
Flack-parameter	-	-	0.473(10)	-
absorpt method	multi-scan	multi-scan	multi-scan	multi-scan
absorpt corr T <sub>min</sub> / <sub>max</sub>	0.6426/0.7456	0.5200/0.7456	0.5025/0.7456	0.5809/0.7456
CCDC No.	1530273	motif	1530274	1530275

 Table S5. Crystal data and refinement details for the X-ray structure determination of the compounds 6-9.

[\*] derived parameters do not contain the contribution of the disordered solvent.<sup>a)</sup> Definition of the *R* indices:  $R_1 = (\Sigma || F_o| + F_c ||)/\Sigma || F_o|;$   $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$  with  $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP;$   $P = [2F_c^2 + Max(F_o^2)/3;$ <sup>b)</sup>  $s = \{\Sigma[w(F_o^2 - F_c^2)^2]/(N_o - N_p)\}^{1/2}$