Electronic supplementary information

From oxide to a new type of molecular tungsten compounds: formation of

bitetrahedral cluster complexes [{W₆(µ₄-O)₂(µ₃-CCN)₄}(CN)₁₆]¹⁰⁻

and $[{W_6(\mu_4-O)_2(\mu_3-As)_4}(CN)_{16}]^{10-}$

Spartak S. Yarovoy,^a Anton I. Smolentsev,^{ab} Svetlana G. Kozlova,^{ab} Nikolay B. Kompankov,^a Yakov M. Gayfulin,^a Igor P. Asanov,^a Vadim V. Yanshole,^{bc} Yuri V. Mironov*^{ab}

^a Nikolaev Institute of Inorganic Chemistry SB RAS, Acad. Lavrentiev ave. 3, 630090 Novosibirsk, Russian Federation. E-mail: yuri@niic.nsc.ru

^b Novosibirsk State University, Pirogova str. 2, 630090 Novosibirsk, Russian Federation

^c International Tomography Center SB RAS, Institutskaya str. 3A, 630090 Novosibirsk, Russian Federation

Table of contents:

- Experimental section: p. S2;
- Crystal data, data collection and refinement parameters for I and II: p. S3-S4;
- The proposed mechanism of CCN3- anion formation: p. S4
- Details of NMR experiments: p. S5-S6;
- Fragment of the ESI mass spectrum of I in aqueous solution, list of cluster products found by the ESI-MS of aqueous solutions of I and II: p. S7-S8;
- Details of XPS experiments: p. S9-S10;
- Details of DFT calculations: p. S11-S15;
- Details of electrochemical investigations: p. S16-S17.
- References: p. S17-S18.

Experimental section

Materials and spectroscopic studies. Electrospray ionization mass spectrometry (ESI-MS) was carried out with a high-resolution accurate mass quadrupole time-of-flight mass spectrometer Bruker maXis 4G (negative ion mode, direct injection with automatic syringe at 180 ul/hour, voltage +2200 V, nebulizer pressure 1 bar, dry gas 4 L/min, dry gas temperature 180 °C). UV/Vis spectra in the wavelength range 200–800 nm were recorded with an Agilent Cary 60 spectrometer. FT-IR spectra in KBr pellets were recorded with a Bruker Scimitar FTS 2000 spectrometer in the range 4000–375 cm⁻¹. Energy dispersion spectroscopy (EDS) was performed by the use of the Hitachi TM-3000 electron microscope equipped with the Bruker Nano EDS analyzer. The elemental analysis of the products using ICP was determined on a high-resolution spectrometer iCAP-6500 (Thermo Scientifc) with a cyclone-type spray chamber and "SeaSpray" nebulizer. The spectra were obtained by axial plasma viewing. Standard operating conditions of the ICP-AES system were following: power = 1150 W, injector inner diameter = 2 mm, carrier argon flow = 0.7 L·min–1, accessorial argon flow = 0.5 L·min–1, cooling argon flow = 12 L·min–1 , number of parallel measurements = 3, and integration time = 5 s. Deionized water (R ≈ 18 MΩ) was used to prepare sample solutions.

 $K_{10}[\{W_6(\mu_4-O)_2(\mu_3-CCN)_4\}(CN)_{16}]\cdot 11H_2O(I)$. WO₃ (0.3 g, 1.29 mmol) and KCN (0.45 g, 6.9 mmol) were pounded in a mortar. The reaction mixture was sealed in an evacuated glass ampoule, heated at 500 °C for 24 h and slowly cooled room temperature. The formed solid was dissolved in boiled water and the resulting brown solution was filtered. Diffusion of methanol vapor into the solution afforded black crystals. Crystals were filtered and dried in air to yield 0.025 g (5%) of product. The addition of red phosphorous (0.04 g, 1.29 mmol) to the reaction mixture before the heating led to increase of the yield up to 15%. Calc. for $K_{10}W_6O_{13}C_{24}N_{20}H_{22}$: K 17.05, W 48.11 %. Found: K 16.25, W 47.97 %. EDS showed a K:W ratio of 9.7:6.0. IR (v, cm⁻¹): 2122 (s, v(CN)), 2178 (m, v(CCN)). UV/vis (H₂O): λ^{max} (ε, mol⁻¹ dm³ cm⁻¹) = 223 (66700), 321 nm (26900).

 $K_{10}[\{W_6(\mu_4-O)_2(\mu_3-As)_4\}(CN)_{16}]\cdot 8H_2O$ (II). WO₃ (0.3 g, 1.29 mmol), As (0.097 g, 1.29 mmol) and KCN (0.45 g, 6.9 mmol) were pounded in a mortar. The reaction mixture was sealed in an evacuated glass ampoule, heated at 500 °C for 24 h and slowly cooled room temperature. The solid was dissolved in boiled water; the resulting brown solution was filtered and left in air for 1 day. The formed black crystalline precipitate was filtered and dried in air to yield 0.194 g (38%) of product. Calc. for K₁₀W₆As₄O₁₀C₁₆N₁₆H₁₆: K 16.39, W 46.23, As 12.56 % Found: K 16.05, W 46.11, As 12.40 %. EDS showed a K:W:As ratio of 9.8:6.0:3.9. IR (v, cm⁻¹): 2100 (s, v(CN)). UV/vis (H₂O): λ^{max} (ε, mol⁻¹ dm³ cm⁻¹) = 244 (sh, 42250), 361 (sh, 12170), 457 nm (sh, 4560).

Single crystal diffraction studies. Crystal structures of I and II were solved by singlecrystal X-ray diffraction analysis. Suitable crystals were selected from the mother liquors, fixed to the tips of glass fibers with epoxy resin, and mounted on a Bruker-Nonius X8 Apex 4K CCD diffractometer (graphite monochromatized Mo-K α radiation, $\lambda = 0.71073$ Å). The X-ray data were collected at 150(2) K by the standard technique (φ - and ω -scans of narrow frames). Data reduction and multi-scan absorption were carried out using the SADABS.¹ The structures were solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELX 2018/3 suite of programs.² All non-hydrogen atoms were refined anisotropically. Hydrogen atoms of solvate water molecules were not located. Crystallographic data and refinement details are given in the Table S1. The complete crystallographic data for I and II have been deposited with the Cambridge Crystallographic data Centre under the reference numbers CCDC 1864684 and 1864685, obtained free of respectively. These data can be charge from CCDC via www.ccdc.cam.ac.uk/structures.

	I	II
Chemical formula	$K_{10}[W_6O_2(CCN)_4(CN)_{16}] \cdot 11H_2O$	$K_{10}[W_6O_2As_4(CN)_{16}] \cdot 8H_2O$
Empirical formula	$C_{24}H_{22}K_{10}N_{20}O_{13}W_6$	$C_{16}H_{16}As_4K_{10}N_{16}O_{10}W_6$
Formula weight	2292.72	2386.23
Temperature (K)	150(2)	150(2)
Crystal size (mm ³)	$0.28 \times 0.10 \times 0.05$	$0.12 \times 0.10 \times 0.02$
Crystal system	Monoclinic	Monoclinic
Space group	$P2_{1}/c$	$P2_{1}/c$
Ζ	4	2
<i>a</i> (Å)	17.8574(5)	11.8440(3)
<i>b</i> (Å)	16.6740(5)	17.5913(4)
<i>c</i> (Å)	22.6906(5)	12.0559(3)
β (°)	126.841(2)	107.0840(10)
$V(Å^3)$	5407.0(3)	2401.03(10)
$D_{\text{calcd.}}$ (g cm ⁻³)	2.816	3.301
μ (Mo K α) (mm ⁻¹)	13.553	17.977
θ range (°)	1.66 – 27.54	1.80 - 30.06
h, k, l indices range	$-23 \le h \le 23;-21 \le k \le 21;-29 \le l \le 20$	$-16 \le h \le 12;$ $-24 \le k \le 23;$ $-16 \le l \le 16$
<i>F</i> (000)	4176	2140

Table S1. Crystal data, data collection and refinement parameters for I and II.

Reflections collected	47393	18389
Unique reflections	12439 ($R_{\rm int} = 0.0495$)	7005 ($R_{\rm int} = 0.0358$)
Observed reflections	9623 [$I > 2\sigma(I)$]	5798 [$I > 2\sigma(I)$]
Parameters refined	658	300
$R[F^2 > 2\sigma(F^2)]$	$R_1 = 0.0348$ $wR_2 = 0.0779$	$R_1 = 0.0337$ $wR_2 = 0.0759$
$R(F^2)$ (all data)	$R_1 = 0.0530$ $wR_2 = 0.0836$	$R_1 = 0.0459$ $wR_2 = 0.0798$
GOOF on F^2	1.049	1.044
$\Delta \rho_{max}, \Delta \rho_{min} (e \text{ Å}^{-3})$	3.116, -2.828	3.304, -2.263

The proposed mechanism of **CCN³⁻** anion formation



Disproportionation of CN-ligand catalyzed by W atom

Scheme S1. The proposed mechanism of CCN³⁻ anion formation.

Nuclear magnetic resonance (NMR) experiments were carried out on the Bruker Avance-III 500 MHz spectrometer at the magnetic fields of B_0 = 11.7 T using a pulse program zg (¹⁷O) and hpdec (¹³C MAS), the interval between the pulses was 0.1 s (¹⁷O) and 120 s (¹³C MAS), the number of scans was 320000 (¹⁷O) and 1024 (¹³C MAS). H₂O and TMS (tetramethylsilane) were used as standards for ¹⁷O and ¹³C NMR, respectively.



Figure S1. ¹⁷O NMR spectra of $[W_6O_2(CCN)_4(CN)_{16}]^{10-}$ (1) and $[W_6O_2As_4(CN)_{12}]^{10-}$ (2) complexes in aqueous solutions. The signal at $\delta \approx 0$ is the ¹⁷O NMR of H₂O.



Figure S2. ¹³C MAS NMR of the solid samples of $K_{10}[W_6O_2(CCN)_4(CN)_{12}] \cdot 11H_2O$ (I) and $K_{10}[W_6O_2As_4(CN)_{12}] \cdot 8H_2O$ (II). The spinning frequency was 15 kHz and 12 kHz, respectively. Insignia (*) are satellite signals.



Figure S3 Fragment of the ESI mass spectrum of I in aqueous solution. Experimental (top) vs calculated (bottom) isotopic distribution peak sets correspond to the anionic adducts $\{K_2[W_6O_2(CCN)_4(CN)_8](H_2O)_2\}^-$ (1), $\{K_2[W_6O_2(CCN)_4(CN)_9](H_2O)_2\}^-$ (2), $\{K_3[W_6O_2(CCN)_4(CN)_9](H_2O)_2\}^-$ (3), ${K_3[W_6O_2(CCN)_4(CN)_{10}](H_2O)_2}^-$ (4), $\{K_3[W_6O_2(CCN)_4(CN)_{10}](H_2O)_3\}^-$ (5), $\{K_4[W_6O_2(CCN)_4(CN)_{10}](H_2O)_2\}^-$ (6) and $\{K_4[W_6O_2(CCN)_4(CN)_{10}](H_2O)_3\}^-$ (7).

Table S2. The experimentally observed maxima of isotopic distribution sets for the adducts and decomposition products of $[W_6O_2(CCN)_4(CN)_{16}]^{10-}$ anion in ESI-MS conditions (negative ion mode, H₂O).

	Anion	m/z	m/z
	Amon	calculated	observed
1	$\{K_2[W_6O_2(CCN)_4(CN)_8](H_2O)_2\}^-$	1609.68	1609.69
2	${K_{2}[W_{6}O_{2}(CCN)_{4}(CN)_{9}](H_{2}O)_{2}}^{-}$	1635.68	1635.69
3	$\{K_3[W_6O_2(CCN)_4(CN)_9](H_2O)_2\}^-$	1674.65	1674.65
4	$\{K_3[W_6O_2(CCN)_4(CN)_{10}](H_2O)_2\}^-$	1700.65	1700.65
5	$\{K_3[W_6O_2(CCN)_4(CN)_{10}](H_2O)_3\}^-$	1718.66	1718.67
6	$\{K_4[W_6O_2(CCN)_4(CN)_{10}](H_2O)_2\}^-$	1739.62	1739.61
7	$\{K_4[W_6O_2(CCN)_4(CN)_{10}](H_2O)_3\}^-$	1757.63	1757.63

Table S3. The experimentally observed maxima of isotopic distribution sets for the adducts and decomposition products of $[W_6O_2As_4(CN)_{16}]^{10-}$ anion in ESI-MS conditions (negative ion mode, H₂O).

Ma	Anion	m/z	m/z
JNG			observed
1	${K[W_6O_2As_4(CN)_9](H_2O)_3}^{2-}$	881.20	881.22
2	${K[W_6O_2As_4(CN)_{10}](H_2O)_3}^{2-}$	894.20	894.22
3	$\{K_2[W_6O_2As_4(CN)_9](H_2O)_3\}^{2-1}$	900.68	900.70
4	$\{K_2[W_6O_2As_4(CN)_{10}](H_2O)_3\}^{2-1}$	913.69	913.70
5	$\{K_2[W_6O_2As_4(CN)_{11}](H_2O)_3\}^{2-1}$	926.69	926.70
6	$\{K_3[W_6O_2As_4(CN)_{11}](H_2O)_3\}^{2-1}$	946.17	946.18
7	$\{K_3[W_6O_2As_4(CN)_{12}](H_2O)_3\}^{2-1}$	959.17	959.18
8	$\{K_4[W_6O_2As_4(CN)_{11}](H_2O)_3\}^{2-1}$	965.65	965.66
9	${K_{4}[W_{6}O_{2}As_{4}(CN)_{12}](H_{2}O)_{3}}^{2}$	978.65	978.67

X-ray photoelectron spectroscopy (XPS) was performed on the SPECS Phoibos-150 MCD spectrometer with a monochromatic Al K α excitation. The electron pass energy was 20 eV. The powder samples were pressed into a double-sided adhesive carbon tape. For neutralization of the charging effect it was applied the irradiation of samples by a low energy electron beam. The calibration of the binding energies was performed relative to an internal standard from the K2p_{3/2} level equal to 293.0 eV. The separation of the contributions from different atoms was carried out by a fitting of spectra on mixed Lorentzian-Gaussian symmetrical components. The C1s and O1s spectra (Figure S3) showed the presence of adventitious surface components probably from the mount tape (strong line at ~285 eV and weak ones at 287 and 289 eV for C1s and 532 and 533 eV for O1s spectra).³ These lines were taken into account for the analysis of the sample spectra. The values of binding energies in the C1s, O1s, N1s, W4f spectra and the standard sample K₆[W₄Te₄(CN)₁₂]·5H₂O are presented in Table S4.

Table S4. The C1s, O1s, N1s, W4f_{7/2} binding energies from the samples I, II and $K_6[W_4Te_4(CN)_{12}]$ ·5H₂O.

Sample	C1s	N1s	W 4f _{7/2}	O1s
$K_{10}[W_6O_2(CCN)_4(CN)_{16}] \cdot 11H_2O(I)$	285.5 (CN, C <u>C</u> N)	398.0 (CN)	32.8 (W(IV))	533.9 (H ₂ O)
	283.7 (<u>C</u> CN)		32.5 (W(III))	530.7 (O ²⁻)
$K_{10}[W_6O_2As_4(CN)_{16}] 8H_2O(II)$	285.6 (CN)	397.8	32.1	534.0 (H ₂ O)
			31.7	530.8 (O ²⁻)
$K_6[W_4Te_4(CN)_{12}] \cdot 5H_2O$	285.4 (CN)	397.8	32.0	534.0 (H ₂ O)



Figure S4. The XPS spectra of compounds $K_6[W_4Te_4(CN)_{12}] \cdot 5H_2O$, I and II at O1s (a) and C1s (b) levels.

Details of DFT calculations. The electronic structure and geometric parameters of the [W₆O₂As₄(CN)₁₆]¹⁰⁻ and [W₆O₂(CCN)₄(CN)₁₆]¹⁰⁻ complexes with D_{2h} symmetry were obtained after optimization procedure by using of the density functional theory method including local density approximation within Vosko-Wilk-Nusair parametrization for local exchange correlations (LDA)⁴ and a generalized gradient approximation (GGA) functional BP86.^{5,6} Standard Slater-type triple- ξ orbital basis sets with two polarization functions (TZP and TZ2P) were used for all atoms.⁷ The zero-order regular approximation (ZORA) Hamiltonian was used in all calculations to take into account the scalar relativistic effects.⁸ Charges on the atoms were calculated by using the Bader method.⁹ All stationary points were characterized as minima (the number of imaginary frequencies (NImag) was equal to zero). Natural bond orbital analysis of 2-center bonds was carried out using the NBO programs implemented in the ADF2017.¹⁰ Nuclear magnetic resonance chemical shifts on oxygen nuclei (¹⁷O NMR) were calculated by using approaches ¹¹⁻¹⁶ with the model potential SAOP.¹⁷ Solvent effects on NMR were simulated by means the conductor-like screening model (COSMO) with water as a solvent using default surface parameters.¹⁸ To compare calculated ¹⁷O NMR chemical shifts (δ_{calc}) with the experimental data (δ_{exp}), we calculated the differences between the magnetic shielding constants on the oxygen nuclei of complexes and water molecules: $\delta_{calc} = -\sigma_{calc}^{compl} + \sigma_{calc}^{stand}$ (where standard is water). The results of quantum-chemical calculations for these complexes: $\sigma_{iso,1} = -13.26$ ppm (I) and $\sigma_{iso,2} = -38.59$ ppm (II), where σ_{iso} is isotropic part of magnetic shielding tensor. The difference in the calculated chemical shifts of ¹⁷O NMR for I and II $\sigma_{iso,1} - \sigma_{iso,2} = 25.3$ ppm is in good agreement with the experimental value $\Delta \delta_{exp}$ $= \delta_{exp,1} - \delta_{exp,2} = 30.4$ ppm.

Atom-Atom	Calc. (I)	Exp. (I)	Calc. (II)	Exp. (II)
$(W_{out}-W_{out}); (W_{in}-W_{in})$	2.893; 2.851	2.768; 2.849	3.132; 2.905	2.809; 2.938
O-W _{in}	2.219	2.184-2.196	2.227	2.184-2.190
O-W _{out}	2.084	1.949-1.956	2.114	1.961-1.974
As-W _{out} ; As-W _{in}	-	-	2.569-2.652	2.511-2.585
W _{out} -C-CN	2.152	2.101-2.192	-	-
C-CN	1.402	1.376-1.400	-	-
CC-N	1.187	1.164-1.186	-	-

Table S5. Selected calculated and experimental interatomic distances (Å) for $[W_6O_2(CCN)_4(CN)_{16}]^{10-}$ (I) and $[W_6O_2As_4(CN)_{16}]^{10-}$ (II) complexes (BP/TZ2P//BP/TZP level).



Figure S5. Optimized geometry and calculated frequencies (IR) of $[W_6O_2As_4(CN)_{16}]^{10}$ - complex under D_{2h} symmetry by using BP/TZ2P level.

Atom	X	Y	Z
1.W	2.110359	1.565826	0.000000
2.C	4.318287	1.831737	0.000000
3.W	2.110359	1.565826	0.000000
4.C	2.493492	3.263049	1.401262
5.W	0.000000	0.000000	1.452416
6.C	2.493492	3.263049	1.401262
7.W	0.000000	0.000000	1.452416
8.0	0.000000	1.687645	0.000000
9.As	2.599379	0.000000	1.977037
10.As	2.599379	0.000000	1.977037
11.N	5.475738	2.091543	0.000000
12.C	4.318287	1.831737	0.000000
13.C	2.493492	3.263049	1.401262
14.C	2.493492	3.263049	1.401262
15.0	0.000000	1.687645	0.000000
16.N	2.816283	4.196555	2.056407
17.W	2.110359	1.565826	0.000000
18.As	2.599379	0.000000	1.977037
19.W	2.110359	1.565826	0.000000
20.C	0.000000	1.350714	3.165574
21.C	0.000000	1.350714	3.165574
22.N	2.816283	4.196555	2.056407
23.As	2.599379	0.000000	1.977037
24.C	0.000000	1.350714	3.165574
25.C	0.000000	1.350714	3.165574
26.C	4.318287	1.831737	0.000000

Table S6.Optimized coordinates (Å	Å) of $[W_6O_2As_4(CN)_{16}]^{10-}$ co	mplex
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27.C	2.493492	3.263049	1.401262
28.C	2.493492	3.263049	1.401262
29.N	5.475738	2.091543	0.000000
30.N	2.816283	4.196555	2.056407
31.N	2.816283	4.196555	2.056407
32.C	4.318287	1.831737	0.000000
33.C	2.493492	3.263049	1.401262
34.C	2.493492	3.263049	1.401262
35.N	0.000000	1.939988	4.192249
36.N	0.000000	1.939988	4.192249
37.N	0.000000	1.939988	4.192249
38.N	0.000000	1.939988	4.192249
39.N	5.475738	2.091543	0.000000
40.N	2.816283	4.196555	2.056407
41.N	2.816283	4.196555	2.056407
42.N	5.475738	2.091543	0.000000
43.N	2.816283	4.196555	2.056407
44.N	2.816283	4.196555	2.056407



Figure S6. Optimized geometry and calculated frequencies (IR) of $[W_6O_2(CCN)_4(CN)_{16}]^{10-}$ complex under D_{2h} symmetry by using BP/TZ2P level.

Atom	X	Y	Z
1.W	0.000000	2.067949	1.446370
2.C	0.000000	4.288918	1.680709
3.W	0.000000	2.067949	1.446370
4.C	1.404325	2.480068	3.165864
5.W	1.425442	0.000000	0.000000
6.C	1.404325	2.480068	3.165864
7.W	1.425442	0.000000	0.000000

Table S7. Optimized coordinates (Å) of $[W_6O_2(CCN)_4(CN)_{16}]^{10-}$ complex

8.O	0.000000	0.000000	1.700955
9.C	1.578342	2.289383	0.000000
10.C	1.578342	2.289383	0.000000
11.N	0.000000	5.437358	1.950118
12.C	0.000000	4.288918	1.680709
13.C	1.404325	2.480068	3.165864
14.C	1.404325	2.480068	3.165864
15.0	0.000000	0.000000	1.700955
16.N	2.023548	2.804475	4.117573
17.W	0.000000	2.067949	1.446370
18.C	1.578342	2.289383	0.000000
19.W	0.000000	2.067949	1.446370
20.C	3.102034	0.000000	1.373860
21.C	3.102034	0.000000	1.373860
22.N	2.023548	2.804475	4.117573
23.C	1.578342	2.289383	0.000000
24.C	3.102034	0.000000	1.373860
25.C	3.102034	0.000000	1.373860
26.C	2.726182	3.093954	0.000000
27.C	2.726182	3.093954	0.000000
28.C	0.000000	4.288918	1.680709
29.C	1.404325	2.480068	3.165864
30.C	1.404325	2.480068	3.165864
31.N	0.000000	5.437358	1.950118
32.N	2.023548	2.804475	4.117573
33.N	2.023548	2.804475	4.117573
34.C	0.000000	4.288918	1.680709
35.C	1.404325	2.480068	3.165864
36.C	1.404325	2.480068	3.165864
37.C	2.726182	3.093954	0.000000
38.N	4.108054	0.000000	1.988639
39.N	4.108054	0.000000	1.988639
40.C	2.726182	3.093954	0.000000
41.N	4.108054	0.000000	1.988639
42.N	4.108054	0.000000	1.988639
43.N	3.680202	3.799800	0.000000
44.N	3.680202	3.799800	0.000000
45.N	0.000000	5.437358	1.950118
46.N	2.023548	2.804475	4.117573
47.N	2.023548	2.804475	4.117573
48.N	3.680202	3.799800	0.000000
49.N	0.000000	5.437358	1.950118
50.N	2.023548	2.804475	4.117573
51.N	2.023548	2.804475	4.117573
52.N	3.680202	3.799800	0.000000

3. Calculated ^{13}C NMR spectra of $[W_6O_2(CCN)_4(CN)_{16}]^{10}$ and $[W_6O_2As_4(CN)_{16}]^{10}$ complexes under D_{2h} symmetry.



Figure S7. Calculated ¹³C NMR spectra of $[W_6O_2(CCN)_4(CN)_{16}]^{10-}$ complex under D_{2h} symmetry.



Figure S8. Calculated ¹³C NMR spectra of $[W_6O_2As_4(CN)_{16}]^{10-}$ complex under D_{2h} symmetry.

Voltammetry. Cyclic voltammetry was carried out on Elins P-20X8 voltammetry analyzer using three-electrode scheme with Pt working, GC auxiliary and Ag/AgCl/3.5M KCl reference electrodes. Differential pulse voltammetry was carried out on Metrohm Computrace 797 VA voltammetry analyzer using the following parameters: pulse amplitude 0.025 V, pulse time 0.02 s, voltage step 0.005951 V, sweep rate 0.003 v s⁻¹. Investigations were carried out for $1.8 \cdot 10^{-2}$ M solutions of **I** or **II** in 0.2M solution of NaCl in H₂O under Ar atmosphere. The evaluation of energy of frontier orbitals was performed for compound **1** using the ferrocene as standard compound with HOMO level lying at -4.8 eV. The following equations were used: HOMO (eV) = $E_{or}(onset, Fc/Fc^+) - E_{or}(onset, sample) - 4.8$; LUMO (eV) = $E_{or}(onset, Fc/Fc^+) - E_{rr}(onset, sample) - 4.8$.^{19, 20}



Figure S9. Cyclic voltammograms of I ((a) 25 mV s_1 scan rate) and II ((b) 100 V s_1 scan rate) in an aqueous solution.



Figure S10. Cyclic voltammogram (red, 25 mV·s⁻¹ scan rate) and differential pulse voltammogram (green, 20 mV·s⁻¹ scan rate) of **I** in aqueous solution.



Figure S11. Cyclic voltammograms of I and II in aqueous solution at different scan rates.

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