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Electrochemically-Switched 2nd Order Non-Linear Optical Response in an Arylimido-Polyoxometalate with High Contrast and Cyclability

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Abstract: Electrochemically switched 2nd order non-linear optical responses have been demonstrated for the first time in polyoxometalates (POMs), with an arylimido-derivative showing a leading combination of high on/off contrast (94%), high visible transparency, and cyclability. Spectro-electrochemical and TD-DFT studies indicate that the switch-off results from weakened charge transfer (CT) character of the electronic transitions in the reduced state. This represents the first study of an imido-POM reduced state, and demonstrates the potential of POM hybrids as electrochemically activated molecular switches.

Since their first observation in the 1960s,^[1] non-linear optical (NLO) effects have become essential to current and future technologies involving generation and manipulation of laser light: for example telecommunications, optical and electro-optical computing, optical data storage and biological imaging.^[2] For advanced applications in telecommunications and computing, the fast 2nd order NLO responses of molecular charge transfer chromophores promise advantages over traditional inorganic salts, and have led to development of many organic and organometallic NLO chromophores.^[2-4] Molecular 2nd order NLO performance is assessed by measurement of the first hyperpolarizability β , with static (zero-frequency) values β_0 used to facilitate comparison. Yet, while materials with extremely high β_0 values ($>>10^{27}$ esu) have been obtained,^[5] only

dimethylaminostilbazolium tosylate (DAST), based on the DAST⁺ cation ($\beta_0 = 25 \times 10^{-30}$ esu),^[3a,b] is in current technological use.

Two key challenges for molecular NLO materials are (i) developing chromophores that combine high activity with adequate transparency,^[6] and (ii) producing materials whose properties can be switched.^[7-9] Regarding (i), structural modifications that increase β usually involve stronger electron donor/acceptor pairs or extended π -systems that increase conjugation – these lower HOMO-LUMO gaps and thus tend to increase absorption of visible and near-infrared light, leading to lower device efficiency and reduced photostability. For (ii), most molecular NLO switches have relied on redox reagents or other chemical stimuli (pH) which are impractical for application in devices,^[7] or photoisomerization^[8] which due to structural change is slower and more vulnerable to side reactions than electron transfer. Electrochemical oxidation of a donor or reduction of an acceptor potentially provides a rapid and device compatible means of switching NLO responses by turning on and off charge transfer transitions,^[9] with less risk of degradation. However, the few existing examples are all based on materials with strong low energy metal-to-ligand charge transfer transitions (MLCT), whose activity is turned off by oxidizing the metal center. Reabsorption of second harmonic light by such MLCT transitions is intrinsically problematic for eventual construction of stable, efficient molecule-based NLO switches.

Herein, we describe a new strategy based on electrochemical switching of higher energy ligand-to-

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polyoxometalate CT (LPCT) transitions. Polyoxometalates (POMs) are well known for fast, stable redox chemistry, as they accept electrons with almost no structural change.^[10] Moreover, owing to push-pull CT effects, we previously demonstrated that NLO chromophores based on arylimido-derivatized Lindqvist POM acceptors ($[\text{Mo}_6\text{O}_{18}\text{NAr}]^{2-}$) show high static first hyperpolarizabilities β_0 , combined with high transparency, giving better transparency/non-linearity trade-offs than typical purely organic systems.^[11] Here, introducing bulky groups (iPr) around the Mo=N bond has enabled us to stabilize and characterise the $[\text{Mo}_6\text{O}_{18}\text{NAr}]^{3-}$ state for the first time, revealing the strongest overall performance of any switchable NLO chromophore to date: $\beta_{0,\text{zzz}} = 89 \times 10^{-30}$ esu (by hyper-Rayleigh Scattering, HRS), high transparency beyond 500 nm, 94% on/off contrast, and the best cyclability yet demonstrated – 4 complete cycles in electrochemistry–HRS, 16 by linear spectroelectrochemistry, with minimal degradation.

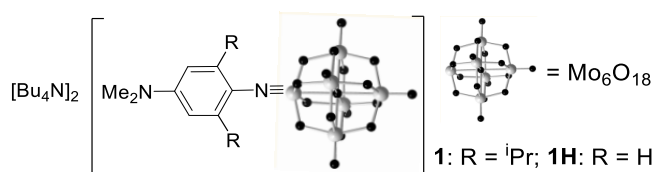


Figure 1. Structures of switchable NLO chromophore $[\text{1}]^{2-}$, and isopropyl-free analogue $[\text{1H}]^{2-}$. $[\text{NBu}_4]_2[\text{1H}]$ was previously published.^[11b]

Donor-acceptor POM derivative $[\text{Mo}_6\text{O}_{18}\text{NPh}(\text{iPr})_2\text{NMe}_2]^{2-}$ ($[\text{1}]^{2-}$, Figure 1) was accessed as a tetrabutylammonium salt following established methods,^[11-13] and thoroughly characterized (see SI, Scheme S1). X-ray quality crystals of $[\text{NBu}_4]_2[\text{1}]\cdot\text{Me}_2\text{CO}$ were obtained, enabling acquisition of a high-quality crystal structure (Figure 2, Table S1).^[14] The Mo-O bond lengths of the cluster are comparable to other hexamolybdate derivatives (Table S2),^[13a,15] while steric repulsion and C-H...O hydrogen bonds (C(H)...O distances ca. 3.3 to 3.7 Å)^[16] between the POM core and the isopropyl groups result in a similar length but more linear imido bond (1.741(1) Å, 175.0(2)°) than observed in other POM-based chromophores.^[11] The slightly less quinoidal structure of the ligand in $[\text{1}]^{2-}$ compared to 2,6-H analogue $[\text{1H}]^{2-}$ (Table S3) suggests slightly weakened donor-acceptor communication.

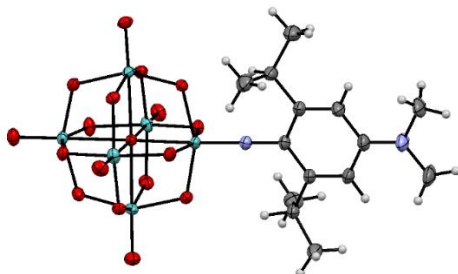


Figure 2. ORTEP representation of the crystal structure of the complex anion $[\text{1}]^{2-}$. C, is grey; N, purple; O, red; and Mo, green, H atoms are white circles with arbitrary radii. Thermal ellipsoids are at the 30% probability level.

Characterization of $[\text{NBu}_4]_2[\text{1}]$ by cyclic voltammetry (CV, Figure S2) finds a $[\text{1}]^{2-/3-}$ reduction peak with near ideal reversibility (Table 1), negatively shifted by ca. 60 mV from that previously reported for $[\text{1H}]^{2-/3-}$.^[11b] This indicates a more electron rich POM cluster, resulting from inductive donation from the iPr

groups ortho to the imido group. A second, irreversible reduction is observed at -1.92 V vs Fc/Fc⁺, while quasi-reversible oxidation of the amine was seen at 0.30 V vs Fc/Fc⁺. UV-vis spectroscopy reveals a ligand-to-POM (LPCT) charge transfer peak at 431 nm (Figure 3, Table 1), slightly redshifted from $[\text{1H}]^{2-}$ (424 nm). This is ascribed to inductive donation from the iPr groups raising the level of the HOMO, which DFT calculations ($\omega\text{B97X-D/6-311G(d)/LanL2TZ}$, MeCN solvation by IEFPCM) indicate is spread across the entire arylimido moiety (Figure 4a), more than the POM based LUMO. TD-DFT calculations reproduce the LPCT peak well, although the (vertical excitation) energy is over-estimated slightly (0.3 eV) vs experiment (Figure S4). The LPCT character of the lowest-energy band is stronger for the oxidised than the reduced form, as shown by the excitation-induced electron density differences (Figure S5). Subsequently, the change of dipole moment upon excitation is slightly smaller for the reduced form than the oxidised one (8.0 versus 9.6 D).

Table 1. UV-vis Absorption and Electrochemical Data for $[\text{1}]^{2-}$ and $[\text{1}]^{3-}$ in MeCN.

Anion	$\lambda_{\text{max}} / \text{nm}^{[\text{a}]}$ (ϵ , $10^3 \text{ M}^{-1} \text{ cm}^{-1}$)	$E_{\text{max}} / \text{eV}$	$E / \text{V vs Fc/Fc}^+ (\Delta E_p / \text{mV})^{[\text{b}]}$		
			$E_{\text{pc}} [\text{1}]^{3-/4-}$	$E_{1/2} [\text{1}]^{2-/3-}$	$E_{1/2} [\text{1}]^{1-/2-}$
$[\text{1}]^{2-}$	206 (44.3)	6.02	-1.92	-1.10 (73)	0.30 (73)
	258 (28.1)	4.81			
	431 (30.7)	2.88			
$[\text{1}]^{3-}$	200 (53.4)	6.20	-1.92	-1.10 (73)	0.30 (73)
	256 (29.4)	4.84			
	398 (25.6)	3.12			

[a] Data for $[\text{1}]^{2-}$ obtained at ca. 10^{-5} M in MeCN. Data for $[\text{1}]^{3-}$ obtained at ca. 10^{-2} M in 0.3 M $[\text{NBu}_4][\text{BF}_4]$ using a thin layer spectroelectrochemistry cell, with initial $[\text{1}]^{2-}$ absorbances as a reference. [b] Solutions ca. 10^{-3} M in analyte, 0.1 M in $[\text{NBu}_4][\text{BF}_4]$ at a glassy carbon working electrode, scan rate 100 mV s^{-1} .

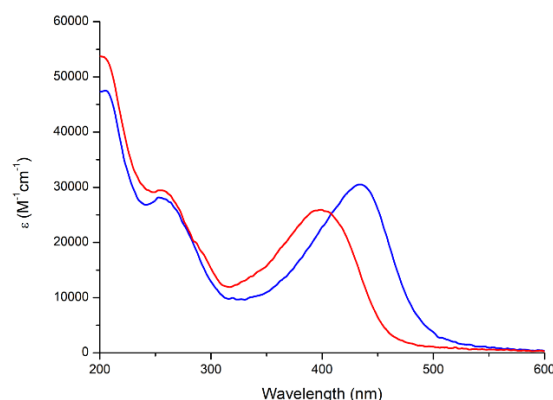


Figure 3 UV-vis spectra of $[\text{1}]^{2-}$ (blue) and $[\text{1}]^{3-}$ (red) obtained by spectroelectrochemistry (electrolyte 0.3 M NBu_4BF_4 in MeCN). 98% recovery of the original spectrum was seen upon re-oxidation.

To probe the stability of the $[\text{1}]^{3-}$ reduced state, and its suitability for redox-switched HRS, we investigated the first reduction of $[\text{1}]^{2-}$ by bulk electrolysis. Investigation of unprotected derivatives such as $[\text{1H}]^{2-}$ in similar conditions has indicated solvolysis of the reduced state leads to loss of ligand and conversion of $\geq 80\%$ of the derivative into $[\text{Mo}_6\text{O}_{19}]^{2-/3-}$.^[17] However, for sterically protected $[\text{NBu}_4]_2[\text{1}]$, CV peak currents measured after 20 minutes reduction at -1.2 V vs Fc/Fc⁺ indicate minimal loss of the imido compound (Figure S3). Subsequent spectroelectrochemical investigation showed that upon reduction the low energy λ_{max} blue

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shifts 33 nm (0.24 eV), to 398 nm, and loses intensity (Figure 3) as the POM acceptor weakens – DFT calculated LUMOs are ca. 0.8 eV higher in energy for the reduced state, consistent with the electrochemically observed spacing of ca. 0.8 V between first and second reductions. TD-DFT calculations fit these observations, showing a blue shift (24 nm, 0.20 eV), and reduction of the intensity, accompanying a lessened LPCT character of the transition (Figures S4/S5). Re-oxidation of the POM core resulted in a 98% recovery of the original sample based on the intensity of the LPCT peak, confirming the stability of the reduced state and the prospects for reversible switching. To further characterize the $[1]^{3-}$ state we performed X-band EPR. At 67 K, this reveals a very similar signal to that of $[\text{Mo}_6\text{O}_{19}]^{3-}$, where an absence of measurable hyperfine coupling indicates delocalization of the electron across the POM cluster. At lower temperatures (10 K), clear evidence of coupling to a single Mo centre, but no large N hyperfine couplings, could be observed (Figure S7). This is consistent with DFT calculations showing a SOMO (slightly stabilized over the α and β HOMOs) based predominantly on the Mo opposite the imido group (Figure 4b), and is logical in showing the electron localizing away from the imido-donor.

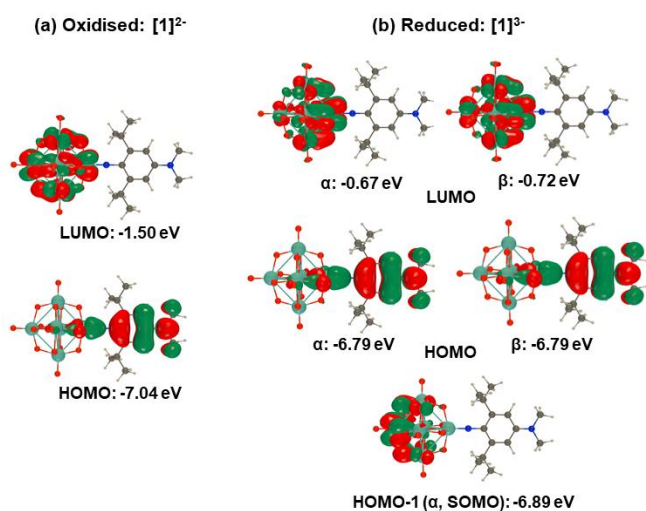


Figure 4. DFT computed frontier orbitals for $[1]^{2-}$ and reduced state $[1]^{3-}$, at the ω B97X-D/6-311G(d)/LanL2TZ level of theory.

Table 2. Comparison of experimental and computational values of hyperpolarizability for $[1]^{2-}$ and its reduced state $[1]^{3-}$.

	$\beta_{1064,\text{HRS}}^{[a]}$	$\beta_{1064,\text{zzz}}^{[a]}$	$\beta_{0,\text{zzz}}^{[a]}$	Computed $\beta_{1064,\text{HRS}}^{[b]}$
$[1]^{2-}$	127.9	309.0	88.8	149.0
$[1]^{3-}$	8.3	20.0	6.7	57.9

[a] Experimental values, $\times 10^{-30}$ esu, $\beta_{0,\text{zzz}}$ calculated from the dynamic hyperpolarizability and the experimental λ_{max} using the two-state model. [b] computational values, $\times 10^{-30}$ esu, after correcting for pre-resonance effects and finite bandwidth of the UV/visible absorption band (see SI).

Hyper-Rayleigh scattering (HRS) performed at 1064 nm revealed a static first hyperpolarizability $\beta_{0,\text{zzz}} = 89 \times 10^{-30}$ esu for $[\text{NBu}_4]_2[1]$ – almost identical to that previously obtained for $[\text{NBu}_4]_2[1\text{H}]$ (Table 2).^[11b] Thus $[1]^{2-}$, like previous “POMophores”, shows a better combination of transparency and activity than

typical purely organic systems – and much better than existing redox switched NLO chromophores, whose activity is based on low energy ($\lambda_{\text{max}} > 500$ nm) MLCT transitions.

A specially designed electrochemical cell (Figure S8, SI) enabled coupled electrochemistry/HRS measurements, which showed a near 94% decrease in second harmonic signal upon reduction of $[1]^{2-}$, and a $\beta_{0,\text{zzz}}$ of only 7×10^{-30} esu for the $[1]^{3-}$ reduced state – a very high contrast switching effect (Figures 5, S9). Reoxidation recovered 90% of the initial signal, which was retained over a further three off/on cycles. The smaller switch-off in later cycles is likely a result of potential drift, as chronoamperometry data reveal less charge was passed and so less complete (ca. 92%) reduction was achieved. The dispersion corrected TD-DFT computed dynamic $\beta_{1064,\text{HRS}}$ value, of 149×10^{-30} esu for $[1]^{2-}$, is a good match for experiment, the calculated reduced state β is a large overestimate, but does reveal an attenuation consistent with the experimental trend. Stability over more cycles has been demonstrated by spectroelectrochemistry, (Figure S10) which shows 95% retention of the absorbance at λ_{max} after 16 cycles. Almost all of the decline occurs in the first 8 cycles, with the absorbance remaining almost constant afterwards. The improved stability in later scans may result from consumption of adventitious water in the first cycles, presence of decomposition products shifting equilibria in favour of $[1]^{2-}/^{3-}$, and also reflects establishment of equilibria between $[1]^{2-}$ and $[1]^{3-}$ after the initial cycles, which may not be completely overcome electrochemically. In any case, the results show that $[1]^{2-}$ is an electrochemically addressable, molecular 2nd order NLO switch with very high contrast and leading multi-cycle stability.^[18]

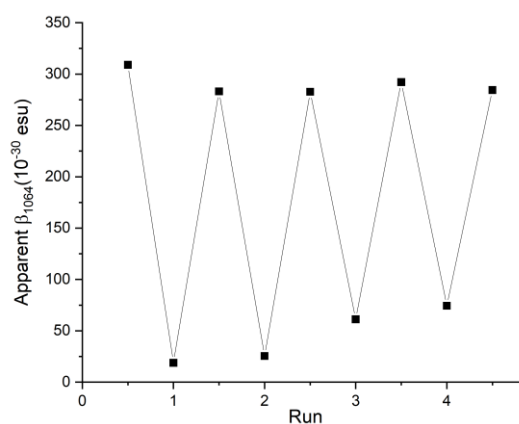


Figure 5. Electrochemically switched HRS signal in $[1]^{2-}$ (on) and $[1]^{3-}$ (off). The smaller “switch off” in runs 3 and 4 is a result of incomplete reduction.

In conclusion, we have shown for the first time that arylimido-Lindqvist reduced states can be effectively stabilized by placing sterically bulky groups around the Mo=N bond. Although the reduced state SOMO is located away from the imido group, reduction dramatically weakens CT to the POM, producing a reversible 94% switch-off in 2nd order NLO activity. Combined with leading cyclability and transparency, this gives $[1]^{2-}$ the best overall performance of any molecular NLO switch to date. Future work will focus on translating these results into thin films,^[9b] to produce bulk materials capable of electrochemical-NLO switching. More broadly, the work highlights the strong potential of imido-POM hybrids as molecular switches, which we are continuing to explore in new structures.

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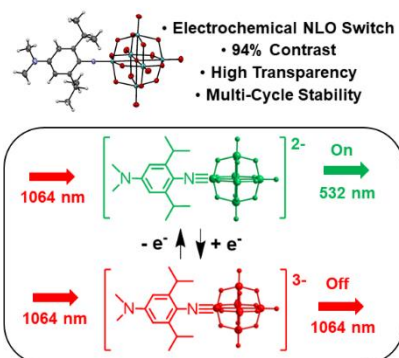
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- [1] P. A. Franken, A. E. Hill, C. W. Peters, G. Weinreich, *Phys. Rev. Lett.* **1961**, *7*, 118.
- [2] (a) *Nonlinear Optics of Organic Molecules and Polymers*; (Eds.: H. S. Nalwa, S. Miyata); CRC Press: Boca Raton, FL, **1997**. (b) S. R. Marder, *Chem. Commun.* **2006**, 131. (c) M. G. Kuzyk, *J. Mater. Chem.* **2009**, *19*, 7444. (d) M. Pawlicki, H. A. Collins, R. G. Denning, H. L. Anderson, *Angew. Chem. Int. Ed.* **2009**, *48*, 3244.
- [3] (a) S. R. Marder, J. W. Perry, W. P. Schaefer, *Science* **1989**, *245*, 626. (b) B. J. Coe, J. A. Harris, I. Asselberghs, K. Clays, G. Olbrechts, A. Persoons, J. T. Hupp, R. C. Johnson, S. J. Coles, M. B. Hursthouse, K. Nakatani, *Adv. Funct. Mater.* **2002**, *12*, 110. (c) B. J. Coe, J. A. Harris, I. Asselberghs, K. Wostyn, K. Clays, A. Persoons, B. S. Brunnschwig, S. J. Coles, T. Gelbrich, M. E. Light, M. B. Hursthouse, K. Nakatani, *Adv. Funct. Mater.* **2003**, *13*, 347. (d) B. J. Coe, J. Fielden, S. P. Foxon, M. Helliwell, I. Asselberghs, K. Clays, K. De Mey, B. S. Brunnschwig, *J. Org. Chem.* **2010**, *75*, 8550. (e) S.-H. Jang, J. Luo, N. M. Tucker, A. Leclercq, E. Zojer, M. A. Haller, T.-D. Kim, J.-W. Kang, K. Firestone, D. Bale, D. Lao, J. B. Benedict, D. Cohen, W. Kaminsky, B. Kahr, J.-L. Brédas, P. Reid, L. R. Dalton, A. K.-Y. Jen, *Chem. Mater.* **2006**, *18*, 2982.
- [4] (a) B. J. Coe, J. Fielden, S. P. Foxon, J. A. Harris, M. Helliwell, B. S. Brunnschwig, I. Asselberghs, K. Clays, J. Garín, J. Orduna, *J. Am. Chem. Soc.* **2010**, *132*, 10498. (b) B. J. Coe, J. Fielden, S. P. Foxon, M. Helliwell, B. S. Brunnschwig, I. Asselberghs, K. Clays, J. Olesiak, K. Matczyszyn, M. Samoc, *J. Phys. Chem. A* **2010**, *114*, 12028. (c) L. T. Cheng, W. Tam, S. H. Stevenson, G. R. Meredith, G. Rikken and S. R. Marder, *J. Phys. Chem.* **1991**, *95*, 10631. (d) L. T. Cheng, W. Tam, S. R. Marder, A. E. Steigman, G. Rikken and C. W. Spangler, *J. Phys. Chem.* **1991**, *95*, 10643.
- [5] (a) H. Xu, F. Liu, D. L. Elder, L. E. Johnson, Y. de Coene, K. Clays, B. H. Robinson, L. R. Dalton, *Chem. Mater.* **2020**, *32*, 1408. (b) H. Xu, L. E. Johnson, Y. de Coene, D. L. Elder, S. R. Hammond, L. R. Dalton, B. H. Robinson, *J. Mater. Chem. C* **2021**, *9*, 2721. (c) H. Xu, D. L. Elder, L. E. Johnson, Y. de Coene, S. R. Hammond, W. V. Ghinst, K. Clays, L. R. Dalton, B. H. Robinson, *Adv. Mater.* **2021**, *33*, 2104174.
- [6] (a) G. Alcaraz, L. Euzenat, O. Mongin, C. Katan, I. Ledoux, J. Zyss, M. Blanchard-Desce, M. Vaultier, *Chem. Commun.* **2003**, 2766. (b) H. Kang, P. Zu, Y. Yang, A. Fchetti, T. J. Marks, *J. Am. Chem. Soc.* **2004**, *126*, 15974. (c) Y. Shi, D. Frattarelli, N. Watanabe, A. Fchetti, E. Cariati, S. Righetto, E. Tordin, C. Zuccaccia, A. Macchioni, S. L. Wegener, C. L. Stern, M. A. Ratner, T. J. Marks, *J. Am. Chem. Soc.* **2015**, *137*, 12521. (d) L. Beverina, A. Sanguineti, G. Battagliarin, R. Ruffo, D. Roberto, S. Righetto, R. Soave, L. L. Presti, R. Ugo, G. A. Pagani, *Chem. Commun.* **2011**, *47*, 292. (e) O. Maury, H. Le Bozec, *Acc. Chem. Res.* **2005**, *38*, 691. (f) H. Xiao, H. Yin, X. Zhang, *Org. Lett.* **2012**, *14*, 5282.
- [7] (a) B. J. Coe, S. Houbrechts, I. Asselberghs, A. Persoons, *Angew. Chem. Int. Ed.* **1999**, *38*, 366. (b) F. Paul, K. Costuas, I. Ledoux, S. Deveau, J. Zyss, J.-F. Halet, C. Lapinte, *Organometallics* **2002**, *21*, 5229. (c) C. Sporer, I. Ratera, D. Ruiz-Molina, Y. Zhao, J. Vidal-Gancedo, K. Wurst, P. Jaitner, K. Clays, A. Persoons, C. Rovira, J. Veciana, *Angew. Chem. Int. Ed.* **2004**, *43*, 5266. (d) P. Kaur, M. Kaur, G. Depotter, S. Van Cleuvenbergen, I. Asselberghs, K. Clays, K. Singh, *J. Mater. Chem.* **2012**, *22*, 10597. (e) S. Di Bella, I. P. Oliveri, A. Colombo, C. Dragonetti, S. Righetto, D. Roberto, *Dalton Trans.* **2012**, *41*, 7013. (f) E. Cariati, X. Liu, Y. Geng, A. Forni, E. Lucenti, S. Righetto, S. Decurtins, S.-X. Liu, *Phys. Chem. Chem. Phys.* **2017**, *19*, 22573. (g) I. Asselberghs, Y. Zhao, K. Clays, A. Persoons, A. Comito, Y. Rubin, *Chem. Phys. Lett.* **2002**, *364*, 279.
- [8] (a) V. Guerschais, L. Ordonneau, H. Le Bozec, *Coord. Chem. Rev.* **2010**, *254*, 2533. (b) K. A. Green, M. P. Cifuentes, M. Samoc, M. G. Humphrey, *Coord. Chem. Rev.* **2011**, *255*, 2530. (c) F. Castet, V. Rodriguez, J.-L. Pozzo, L. Ducasse, A. Plaquet, B. Champagne, *Acc. Chem. Res.* **2013**, *46*, 2656. (d) J. Boixel, V. Guerschais, H. Le Bozec, D. Jacquemin, A. Amar, A. Boucekkine, A. Colombo, C. Dragonetti, D. Marinotto, D. Roberto, S. Righetto, R. De Angelis, *J. Am. Chem. Soc.* **2014**, *136*, 5367. (e) P. Beaujean, F. Bondu, A. Plaquet, J. Garcia-Amorós, J. Cusido, F. M. Raymo, F. Castet, V. Rodriguez, B. Champagne, *J. Am. Chem. Soc.* **2016**, *138*, 5052.
- [9] (a) I. Asselberghs, K. Clays, A. Persoons, A. M. McDonagh, M. D. Ward, J. A. McCleverty, *Chem. Phys. Lett.* **2003**, *368*, 408. (b) L. Boubekeur-Lecaque, B. J. Coe, K. Clays, S. Foerier, T. Verbiest, I. Asselberghs, *J. Am. Chem. Soc.* **2008**, *130*, 3286. (c) C. Karthika, S. R. Sarath Kumar, L. Kathuria, P. K. Das, A. G. Samuelson, *Phys. Chem. Chem. Phys.* **2019**, *21*, 11079.
- [10] (a) M. Sadakane, E. Steckhan, *Chem. Rev.* **1998**, *98*, 219.
- [11] (a) A. Al-Yasari, N. Van Steerteghem, H. El Moll, K. Clays, J. Fielden, *Dalton Trans.* **2016**, *45*, 2818. (b) A. Al-Yasari, N. Van Steerteghem, H. Kearns, H. El Moll, K. Faulds, J. A. Wright, B. S. Brunnschwig, K. Clays, J. Fielden, *Inorg. Chem.* **2017**, *17*, 10181. (c) A. Al-Yasari, P. Spence, H. El Moll, N. Van Steerteghem, P. N. Horton, B. S. Brunnschwig, K. Clays, J. Fielden, *Dalton Trans.* **2018**, *47*, 10415; E. Rtibi, M. Abderrabba, S. Ayadi, B. Champagne, *Inorg. Chem.* **2019**, *58*, 11210.
- [12] F. J. Carver, C. A. Hunter, D. J. Livingstone, J. F. McCabe, E. M. Seward, *Chem. Eur. J.* **2002**, *8*, 2847.
- [13] (a) Y. Wei, B. Xu, C. L. Barnes and Z. Peng, *J. Am. Chem. Soc.* **2001**, *123*, 4083. (b) I. Bar-Nahum, K. V. Narasimulu, L. Weiner, R. Neumann, *Inorg. Chem.* **2005**, *44*, 4900.
- [14] Deposition Number 2214337 contains the supplementary crystallographic data for this paper. These data are provided free of charge by the joint [Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service](https://www.ccdc.cam.ac.uk/).
- [15] (a) J. B. Strong, G. P. A. Yap, R. Ostrander, L. M. Liable-Sands, A. L. Rheingold, R. Thouvenot, P. Gouzerh, E. A. Maatta, *J. Am. Chem. Soc.* **2000**, *122*, 639. (b) B. Xu, Y. Wei, C. L. Barnes, Z. Peng, *Angew. Chem. Int. Ed.* **2001**, *40*, 2290.
- [16] A. Al-Yasari, H. El Moll, R. Purdy, Kevin B. Vincent, P. Spence, J.-P. Malval, J. Fielden, *Phys. Chem. Chem. Phys.* **2021**, *23*, 11807.
- [17] A. Al-Yasari, Ph.D Thesis, University of East Anglia, **2016**.
- [18] Previously, a maximum of 3 complete on/off cycles have been demonstrated by electrochemistry or redox switching (ref 7f), and 4 complete cycles by photo-switching (ref 8d) albeit with steady deterioration of the on-state signal.

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Charge transfer transitions in a new arylimido-polyoxometalate (POM) are turned off by reduction, enabling a high contrast (94%) electrochemically switched 2nd order non-linear optical (NLO) response. The overall combination of on/off contrast, high visible transparency and multicycle stability is leading in switchable 2nd order NLO chromophores, and shows for the first time the strong potential of POM hybrids as redox-driven optical switches.

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