Communication

John Fielden et al.
Fine-tuning polyoxometalate non-linear optical chromophores: a molecular electronic “Goldilocks” effect
Fine-tuning polyoxometalate non-linear optical chromophores: a molecular electronic “Goldilocks” effect†

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A new aryl-imido polyoxometalate non-linear optical chromophore (POMophore) with a diphenylamino donor group attains the highest βesr α value (196 × 10−30 esu by Hyper-Rayleigh Scattering, HRS), and best transparency/non-linearity trade off yet for such materials. Stark spectroscopic and DFT investigation of this compound, plus NMe2 and carbazole analogues, show that its high performance results from a combination of strongly dipolar electronic transitions, and strong electronic communication across the π-system. The chemistry of covalent polyoxometalate (POM) “hybrid” compounds has advanced rapidly in recent years. Organic groups can be connected to many of the common POM cluster anions, and an increasing range of post-synthetic modifications enable incorporation of POMs into complex organic architectures. However, study of the physical properties, and associated applications of these structures is still in its infancy. Relatively little is known about the interaction between the POM and organic subunit, and indeed in most systems electronic communication between them appears to be weak.

With strong electronic communication between an acceptor (e.g. a POM) and more electron rich moieties, many useful optical and photophysical properties can emerge – such as non-linear optical (NLO) effects. NLO materials are used to manipulate laser light, and the tunable properties and strong, fast responses associated with molecular donor–acceptor systems (vs. traditional extended inorganic solids) is critical to development of advanced applications in telecommunications, optical/electro-optical computing and imaging. We recently showed that the strong POM-organic communication in donor-functionalized arylimido-Lindqvist ([Mo6O19]2−) anions results in promising 2nd order NLO (laser frequency doubling) properties. Specifically, these POM acceptors combined with short (phenyl) π-bridges give rise to a better combination of transparency and 2nd order NLO activity than planar, dipolar organic systems. Thus, they may help overcome the challenge of obtaining materials that have high NLO coefficients (β), while avoiding problems for efficiency and stability that result from reabsorption of second harmonic (SH) light. As yet though, absolute β-values for these POMophores fall far short of records and extension of the organic π-system – a classic means of increasing β – has been seen to sacrifice any advantage over purely organic (nitro) analogues.

Herein, we investigate the effect of using the weaker, but more conjugated donor groups carbazole (cbz) and diphenylamino (NPh2) on the behaviour of extended POMophores. We find that, of the donor groups tested so far, NPh2 is the best adapted for use in POMophores – producing the highest β and best transparency/non-linearity trade-off. This results from a combination of stronger electronic communication, and strong, relatively high energy electronic transitions that maintain a highly dipolar nature.

The synthetic approach to 1 to 3 (Fig. 1) centres on the DCC-mediated coupling of anilines with [NBu4][Mo6O19]. For both 1 and 2, we found the most expeditious route was to first synthesize the precursor diphenylamino and cbz functionalized ligands, before reaction with hexamolybdate. The syn-

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thesis of 3 was previously published.\textsuperscript{5b} Notably, both 1 and 2 (most of all 2) are more vulnerable to hydrolysis than 3 and other previously studied arylimido-POMs (a-POMs), and require careful handling. As there is no difference in steric protection of the imido-bond, this observation implies a difference in electronic structure that increases its reactivity. UV-vis spectra (Table 1, Fig. S1 in ESI\textsuperscript{†}) show that compared to 3, these compounds both show blue shifts in \(E_{\text{max}}\) of the intra-hybrid charge transfer (HCT\textsuperscript{5b}) band, consistent with their weaker electron donors. However, they also absorb more strongly across the range from 300 to 400 nm, likely a result of stronger \(\pi\)-conjugation. Despite the weaker donors, the reduction potentials of the \([\text{Mo}_6]\) unit in 1 and 2 are at a similar potential to that of 3 (Table 1), suggesting that communication between the POM and NMe\(_2\) donor is weaker than with NPh\(_2\) or cbz.

HRS-determined \(\beta\)-values for 1 to 3 are shown in Table 2. For 1, the higher value obtained at 1100 nm is likely more accurate, as at 1064 nm the analysis was complicated by a need to deconvolute HRS and fluorescence signal. Even so, both resonance corrected static \(\beta\)-values (\(\beta_0\)) for 1 are substantially lower than that of 3, commensurate with the lower donor strength. For 2, \(\beta_0\) is around 40\% higher than for 3, and combined with its lower \(\lambda_{\text{max}}\) this makes it the best performing POMophore described to date. Compound 2 is also the first extended POMophore that clearly outperforms comparable purely organic systems, as shown by an intrinsic \(\beta\) value that breaks through empirical performance limits (defined by intrinsic \(\beta\) vs. \(\lambda_{\text{max}}\) defined by Kuzyk for planar, dipolar organics (Fig. 2).\textsuperscript{7} Although POM electrons are not included in the N used to calculate intrinsic \(\beta\), this analysis clearly shows that the POM must influence the NLO properties of the organic system. Moreover, the POM is broadly analogous to the aryl remote acceptor in N-aryl stilbazolium chromophores – the electrons of this aryl group are not included in N for these systems, and yet N-aryl stilbazoliums do not exceed the apparent limit in Fig. 2.\textsuperscript{7b}

Thus, it appears that the POM contributes more to the NLO properties of 2, than it does to those of 3, leading to a reversal of the trend seen for structurally analogous systems with the NO\(_2\) acceptor,\textsuperscript{8} where NMe\(_2\) outperforms NPh\(_2\) with both alkyne and alkene bridges. This suggests that the POM acceptor must alter the electronic structure of the organic donor and bridge, and since NPh\(_2\) is a weaker donor than NMe\(_2\), it must increase \(\beta\) by influencing charge separation and communication across the bridge. Indeed, the X-ray crystal structures of both 1 and 2 vs. 3 (Fig. 3, see ESI\textsuperscript{†} for full details) are consistent with stronger conjugation. Whereas that of 3 shows a ca. 86° twist between the planes of the two phenyl rings,\textsuperscript{5b} in

| \(\lambda_{\text{max}}\) (nm) | \(E_{\text{max}}\) (eV) | Assignment | \(E_{1/2}\) vs. Ag/AgCl/\(\Gamma^+\) (\(\Delta E\)/mV) |
|-----------------|-----------------|-------------|---------------------|
| 1               | 227 (70.4)      | 5.28        | O → Mo and \(\pi\) → \(\pi^*\) | -0.503 (64) |
|                 | 292 (48.4)      | 4.25        | O → Mo and \(\pi\) → \(\pi^*\) |                  |
|                 | 327 (31.3)      | 3.78        | O → Mo and \(\pi\) → \(\pi^*\) |                  |
|                 | 341 (33.7)      | 3.63        | O → Mo and \(\pi\) → \(\pi^*\) |                  |
|                 | 385 (43.4)      | 3.20        | IHCT                 |                  |
| 2               | 292 (41.2)      | 4.28        | O → Mo and \(\pi\) → \(\pi^*\) | -0.503 (64) |
|                 | 337 (36.2)      | 3.74        | O → Mo and \(\pi\) → \(\pi^*\) |                  |
|                 | 414 (45.3)      | 2.98        | IHCT                 |                  |
| 3               | 248 (36.2)      | 5.02        | O → Mo and \(\pi\) → \(\pi^*\) | -0.498 (61) |
|                 | 292 (44.5)      | 4.24        | O → Mo and \(\pi\) → \(\pi^*\) |                  |
|                 | 421 (41.2)      | 2.94        | IHCT                 |                  |

\(a\) Concentrations ca. 10\textsuperscript{-3} M in MeCN. \(b\) Solutions ca. 10\textsuperscript{-3} M in analyte and 0.1 M in [NBu\(_4\)][BF\(_4\)] at a glassy carbon working electrode with a scan rate of 100 mV \textsuperscript{-1}. Ferrocene internal reference \(E_{1/2} = 0.46\) V, \(\Delta E_p = 80\) mV. Data for 3 are from ref. 5b.
2 this is only \(ca.\) 22°, and in \(1\) 19°. Moreover, the imido (acceptor) ring in \(2\) shows a shortening of the ortho- to meta- \(C-C\) bonds (mean distance 1.36(2) Å vs. 1.42(2) Å for ortho/meta-to-

**Fig. 3** (a) ORTEP representation of the molecular anions in \(1\) and \(2\). Disordered parts omitted for clarity, thermal ellipsoids are at the 30% probability level, C atoms are grey; Mo; green; O; red; N; blue. H atoms are white spheres of arbitrary radii. (b) Crystal packing in \(2\) viewed along the crystallographic \(a\)-axis. For clarity, \(\text{NBu}_4^+\) cations are colored blue and \([\text{Mo}_{6}\text{O}18\text{NPhCCPhNPh}_2]\)^{2-} anions are colored green.

**Fig. 4** TDDFT calculated HOMOs for \(1\) to \(3\) (bottom) and most important acceptor orbitals LUMO+\(x\) (in terms of oscillator strength topl).

band (16 to 35 nm). This can be an indicator of dipolar electronic transitions.\(^{10}\) The Stark-derived \(\Sigma\beta_0\) values for the series (Table 3, see ESI for details of fitting and extraction of charge transfer parameters) follow a similar trend to HRS \(\beta_0\), although measurement and fitting uncertainties are large and in all cases values are larger than HRS \(\beta_0\) – a common observation in prior work.\(^{5b,7,11}\) Similar to \(3\), the fit of the main low energy peak in \(2\) consists of three Gaussians, each at slightly higher energy than those of \(3\). Dipole moment changes \(\Delta\mu\) and charge transfer distances \(r\) associated with these peaks in \(2\) and \(3\) are within experimental error of one another (though consistently slightly higher for \(2\)), as are most other measured parameters. However, an additional peak in \(2\) requires a \(4\)^th Gaussian for an adequate fit, and while its transition is less dipolar in nature (lower \(\Delta\mu\) values) it shows strong electronic coupling (higher \(H_{ab}\)) and a high value of \(\mu_{zzz}\) means that it contributes significantly to \(\Sigma\beta_0\). In \(1\), the four Gaussian components have less dipolar character their counterparts in \(1\) and \(3\), and generally electronic coupling is stronger than in either \(2\) or \(3\). The overall picture suggests that \(2\) hits a sweet spot where transitions are just as dipolar than those of \(3\), yet electronic communication across the diphenylacetylene bridge is strong.

TDDFT calculations of the electronic spectra and \(\beta\) values of \(1\) to \(3\) in acetonitrile solvent have been performed using the ADF program, with the SAOP functional and TZ2P basis set. Previously,\(^5\) we showed that a solvent forcefield is necessary for these calculations to reflect experimental trends, although the \(\beta\) values computed were much larger (up to \(30\times\) than those observed experimentally. The methods used here are an incremental improvement on those previously published. Values are closer to experiment, but still high (reflecting low computed transition energies, see ESI), and the trend is an excellent match for Stark and HRS findings. \(\beta_{zzz}, 0\) of 960 (1), 1300 (3) and 2160 \(\times\) \(10^{-3}\) (2) are obtained, and normalising all three techniques to \(2\) as 100% (Table S2\(^\dagger\)) makes it clear just how good the agreement in trend is between experiment and theory. A qualitative interpretation of the TDDFT-computed orbital-to-orbital transitions is thus justified, and reveals two key differences between \(2\) and \(3\). Firstly, the HOMO level of \(2\) is concentrated on the NPh2 group and immediately appended aryl ring (Fig. 4), whereas in \(3\) it spreads across the entire organic system – as does the HOMO–1 for both systems. This may increase the dipole moment change associated with strong, low energy transitions to the LUMO+6 and LUMO+8, which spread across POM and imido-ring, and is reflected in the very slightly higher \(\Delta\mu\) values found for \(2\) by Stark (although they are within experimental error of those for \(3\)). Secondly, \(3\) has a weak transition from an imido-phenyl based HOMO–5, to a POM-based LUMO+7, at a high computed energy (3.39 eV, Table S5 and Fig. S7\(^\dagger\)). In \(2\), a similar transition is observed from the HOMO–9 to LUMO+1 (Table S4 and Fig. S6\(^\dagger\)), but the calculated energy is 0.7 eV lower and calculated \(f_{ab}\) nearly \(3\times\) higher – possibly due to involvement of the alkylene bridge. This seems consistent with the fourth Gaussian peak used to fit the Stark spectrum of \(2\), which has both moderately high \(H_{ab}\) and \(\Delta\mu\), and appears responsible for...
In butyronitrile at 77 K; observed absorption maxima with maxima for Gaussian fitting functions in brackets. Data in all subsequent columns relate to fitted curves. Obtained from \((4.6 \times 10^{-9} \text{ M cm}^3)\) \(\epsilon_{\text{max}} \times f_{\text{whh}}\) where \(\epsilon_{\text{max}}\) is the maximal molar extinction coefficient and \(f_{\text{whh}}\) is the full width at half height (in cm\(^{-1}\)). Calculated using eqn (2), ESI. Calculated from \(f_{\text{simp}} \Delta \mu_{12}\) using \(f_{\text{simp}} = 1.33\). Calculated from eqn (1), ESI. Effective (localized) electron-transfer distance calculated from \(\Delta \mu_{12}/c\). Calculated using eqn (3), ESI. Calculated from eqn (4), ESI. Calculated from eqn (5), ESI. Sum of the \(\beta_0\) values from each individual Gaussian function, to 2 s.f. Estimated errors are ca. \(\pm 20\%\) on \(\beta_0\), \(\mu_{12}\) and \(\Delta \mu_{12}\), \(\pm 30\%\) on \(H_{ab}\), and \(\pm 50\%\) \(c_0^b\) and are further discussed in the ESI.

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In addition to the supplementary information and deposited cif files, data can be accessed by contacting the corresponding author.

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