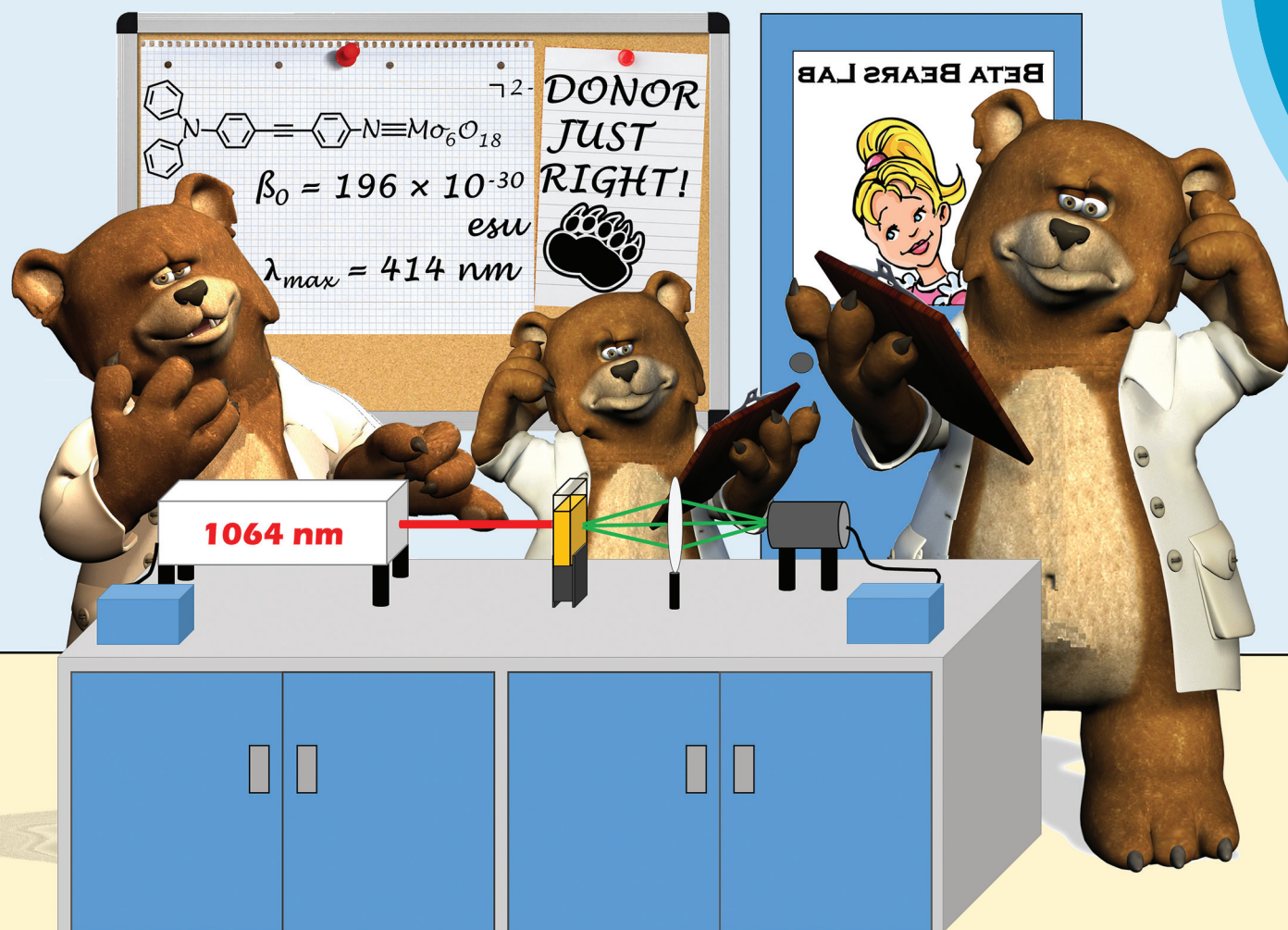


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Fine-tuning polyoxometalate non-linear optical chromophores: a molecular electronic “Goldilocks” effect†

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A new aryl-imido polyoxometalate non-linear optical chromophore (POMophore) with a diphenylamino donor group attains the highest $\beta_{zzz, 0}$ 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.¹ However, study of the physical properties,² and associated applications³ 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.⁴ 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.⁵ 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.^{5b}

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_0 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]₂[Mo₆O₁₉].^{1c,5} 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-

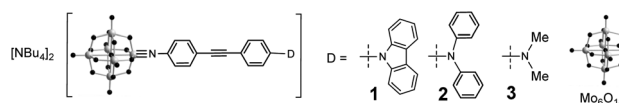


Fig. 1 Arylimido Lindqvist based chromophores **1** to **3**.

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thesis of **3** was previously published.^{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†) show that compared to **3**, these compounds both show blue shifts in E_{\max} of the intra-hybrid charge transfer (IHCT^{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 π -conjugation. Despite the weaker donors, the reduction potentials of the {Mo₆} unit in **1** and **2** are at a similar potential to that of **3** (Table 1), suggesting that communication between the POM and NMe₂ donor is weaker than with NPh₂ or cbz.

HRS-determined β -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 β -values (β_0) for **1** are substantially lower than that of **3**, commensurate with the lower donor strength. For **2**, β_0 is around 40% higher than for **3**, and combined with its lower λ_{\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 β value that breaks through empirical performance limits (defined by intrinsic β vs. λ_{\max}) defined by Kuzyk for planar, dipolar organics (Fig. 2).⁷ Although POM electrons are not included in the N used to calculate intrinsic β , 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.^{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

Table 2 HRS data at 1064 and 1100 nm for **1** to **3**

λ_{\max} (nm)	$\beta_{\text{zzz}, 1064}^a$ (10^{-30} esu)	$\beta_0, 1064^b$	$\beta_{\text{zzz}, 1100}^a$	$\beta_0, 1100^b$	$\beta_0/N^{3/2}{}^c$
1 388	150 ± 36	62 ± 15	190 ± 28	82 ± 12	1.57
2 415	590 ± 20	196 ± 7	—	—	3.75
3 421	440 ± 55	139 ± 17	—	—	2.65

^a β_{zzz} calculated assuming a single dominant tensor component, measured using 1064 or 1100 nm fundamental laser beams. The quoted units (esu) can be converted into SI units ($\text{C}^3 \text{m}^3 \text{J}^{-2}$) by dividing by a factor of 2.693×10^{20} . ^b Non-resonant, static β estimated from β_{zzz} using the two state model.⁶ Data for **3** are from ref. 5b. ^c N = number of π -electrons in bridge.⁷

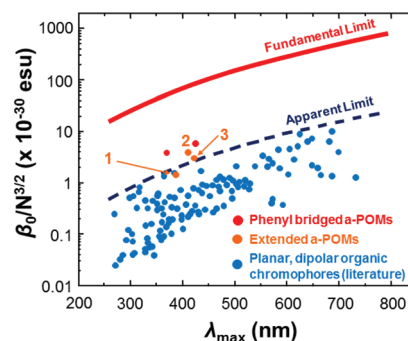


Fig. 2 Intrinsic β vs. λ_{\max} for **1**, **2** and **3** vs. short (phenyl bridged) POMophores,⁵ and planar, dipolar organic chromophores.⁷ Compound **2** is the first POMophore to clearly breach Kuzyk's apparent limit for the performance of planar, dipolar organic chromophores.

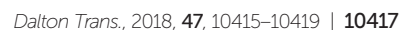
NO₂ acceptor,⁸ where NMe₂ outperforms NPh₂ with both alkyne and alkene bridges. This suggests that the POM acceptor must alter the electronic structure of the organic donor and bridge, and since NPh₂ is a weaker donor than NMe₂, it must increase β by influencing charge separation and communication across the bridge. Indeed, the X-ray crystal structures of both **1** and **2** vs. **3** (Fig. 3, see ESI† 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,^{5b} in

Table 1 UV-vis absorption and electrochemical data for **1** to **3** in acetonitrile

	$\lambda_{\max}/\text{nm}^a$ (ϵ , $10^3 \text{ M}^{-1} \text{ cm}^{-1}$)	E_{\max} (eV)	Assignment	$E_{1/2}$ vs. Ag/AgCl/ V^b ($\Delta E/\text{mV}$)
1	227 (70.4)	5.28	O → Mo and $\pi \rightarrow \pi^*$	−0.503 (64)
	292 (48.4)	4.25	O → Mo and $\pi \rightarrow \pi^*$	
	327 (31.3)	3.78	O → Mo and $\pi \rightarrow \pi^*$	
	341 (33.7)	3.63	O → Mo and $\pi \rightarrow \pi^*$	
	385 (43.4)	3.20	IHCT	
2	292 (41.2)	4.28	O → Mo and $\pi \rightarrow \pi^*$	−0.503 (64)
	327 (36.2)	3.74	O → Mo and $\pi \rightarrow \pi^*$	
	414 (45.3)	2.98	IHCT	
	248 (36.2)	5.02	O → Mo and $\pi \rightarrow \pi^*$	
3	292 (44.5)	4.24	O → Mo and $\pi \rightarrow \pi^*$	−0.498 (61)
	421 (41.2)	2.94	IHCT	

^a Concentrations *ca.* 10^{-5} M in MeCN. ^b Solutions *ca.* 10^{-3} M in analyte and 0.1 M in [NBu₄][BF₄] at a glassy carbon working electrode with a scan rate of 100 mV s^{−1}. Ferrocene internal reference $E_{1/2} = 0.46$ V, $\Delta E_p = 80$ mV. Data for **3** are from ref. 5b.





	λ_{\max}^a (nm)	E_{\max}^a (eV)	Amp (norm)	Fwhh (eV)	f_{os}^b	μ_{12}^c (D)	$\Delta\mu_{12}^d$ (D)	$\Delta\mu_{\text{ab}}^e$ (D)	r_{12}^f (Å)	r_{ab}^g (Å)	H_{ab}^h (10^3 cm^{-1})	$c_{\text{b}}^{2,i}$	β_0^j (10^{-30} esu)	$\Sigma\beta_0^k$ (10^{-30} esu)
1	404 (433)	3.07 (2.86)	0.13	0.16	0.06	2.4	12.5	13.4	2.6	2.8	4.2	0.97	11	180
	(405)	(3.06)	0.56	0.44	0.82	8.4	17.7	24.4	3.7	5.1	8.5	0.87	155	
	(366)	(3.39)	0.16	0.28	0.16	3.6	9.1	11.6	1.9	2.4	8.4	0.90	12	
	(342)	(3.62)	0.15	0.28	0.16	3.4	—	—	—	—	—	—	0	
2	444 (475)	2.79 (2.61)	0.22	0.18	0.13	3.6	22.5	23.7	4.7	4.9	3.2	0.98	51	350
	(451)	(2.75)	0.29	0.28	0.28	5.2	24.2	26.3	5.0	5.5	4.4	0.96	101	
	(425)	(2.92)	0.30	0.42	0.46	6.4	25.0	28.1	5.2	5.9	5.4	0.94	142	
	(355)	(3.50)	0.20	0.55	0.51	6.2	15.8	20.0	3.3	4.2	8.7	0.90	57	
3	456 (482)	2.72 (2.57)	0.30	0.20	0.16	4.0	21.6	23.1	4.5	4.8	3.7	0.97	64	280
	(456)	(2.72)	0.41	0.28	0.34	5.7	23.3	26.0	4.9	5.4	4.9	0.95	121	
	(426)	(2.91)	0.29	0.35	0.31	5.3	24.6	26.8	5.1	5.6	4.7	0.96	96	

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