From red to blue shift: switching the binding affinity from the acceptor to the donor end by increasing the π-bridge in push–pull chromophores with coordinative ends†

Marco Caricato,[a] Carmine Coluccini,[a] Douglas A. Vander Griend,[b] Alessandra Forni[c] and Dario Pasini*[ad]

A series of homologous push–pull compounds, in which identical donor (a dimethylamino) and acceptor (a malonate ester) functionalities endcap crescent PPV fragments, exhibit striking differences in their supramolecular recognition of cations acting as Lewis acids. The shorter conjugated compound (one phenyl ring) coordinates a wide variety of lanthanide cations (Eu^{3+}, Yb^{3+} and Er^{3+}) in MeCN solutions to the 1,3-dicarbonyl acceptor end, resulting in an overall supramolecular polarization of the system (red shift of the intramolecular charge-transfer ICT band). With the ''hard'' cation Sc^{3+}, recognition switches to the tertiary amine donor end, turning the conjugated system from D–π–A to A–π–A, and resulting in a blue shift of the ICT band upon complexation. Interestingly, increasing the conjugation by means of the insertion of sequential *p*-phenylenevinylene units into the ligand results in coordination to the donor end regardless of cation ''hardness'' (Sc^{3+}, Eu^{3+} and Er^{3+}), suggesting a relative change in the nucleophilicity of the two coordinating ends when increasing the length of the conjugated π-bridge. Such a hypothesis is supported by quantum chemical calculations on the ligands and subsequent atomic charges determination using two independent approaches (QTAIM and CHelpG). The characterization of the thermodynamic stabilities and the dimensionalities of the ligand–cation complexes in solution reveals striking differences from case to case, yet increasing affinities (from $\log K_{av} = 2.5$ to $\log K_{av} = 4.9$) are recorded with the increase of the π-conjugated bridge.

Introduction

Soluble, processable *p*-phenylenevinylene oligomers (OPVs) have been in the last few decades extensively studied for several applications;[1] in fact, they can be useful models for the understanding of the solution and bulk scale properties of the corresponding polymers.[2] The insertion of suitable electron-withdrawing or electron-donating substituents in direct conjugation with the π-extended backbone, in order to tailor the electronic properties, has been thoroughly addressed through chemical synthesis;[1] changes in shape and structure, to form cruciforms,[3] dendrimers,[4] and paracyclophanes,[5] have also been recently reported.

The ability to modify the electronic properties of the π-extended chromophores by a supramolecular coordination event is of great interest. In an extensive interpretation, this concept has been developed mainly in the design of molecular sensors (using the changes in the electrochemical/emission properties of the conjugated moiety upon complexation in order to sense the analyte),[6] and, less frequently, using specific substrates supramolecularly bound to the π-extended backbone, to tune the electrooptic response.[7]

We have recently reported on the characterization of supramolecular complexes involving push–pull chromophores in which the electron-withdrawing molecular fragment is a malonate moiety, and we have demonstrated that this moiety is able to form supramolecular, reversible complexes with metal cations (such as lanthanides) behaving as Lewis acids.[8]

[a] *Department of Chemistry, University of Pavia, Viale Taramelli, 10-27100 Pavia, Italy. E-mail: dario.pasini@unipv.it; Web: www.unipv.it/labt; Fax: +39 0382 987323; Tel: +39 0382 987835*

[b] *Department of Chemistry & Biochemistry, Calvin College, Grand Rapids, MI 49546-4403, USA*

[c] *Institute of Molecular Sciences and Technologies (ISTM), CNR, Via Golgi 19, 20133 Milano, Italy*

[d] *INSTM Research Unit, University of Pavia, Italy*

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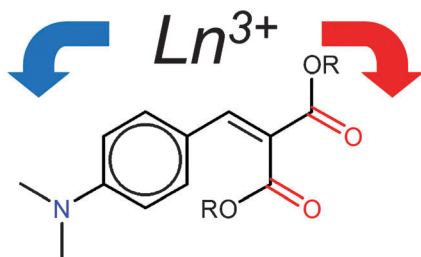
Fig. 1 Complexation induced red or blue shift of the ICT band in ''push–pull'' chromophores.

The peculiar nature of these complexes is testified by a large red shift (380 → 480 nm) of the intramolecular charge-transfer absorption band (ICT) upon complexation (Fig. 1).[8a] Alongside such prototypical compounds (methyl ester of structure shown in Fig. 1), the red shift of the ICT band upon metal ion complexation has been demonstrated for structurally identical chromophores embedded in a wide series of molecular architectures. These molecular architectures include malonate crown ether derivatives, in which oligoethylene chains bridge as esters the two carbonyl appendices of the malonate group, double chromophoric systems, and chromophores embedded into cyclopolymeric systems.[8] Other π-donating functionalities have been tested (alkoxy, ferrocene derivatives), but the 4-dimethylamino derivatives showed by far the largest ICT response.

1,3-Dicarbonyl units (either ketones or esters, such as acetylacetone, for example) are commonly used as bidentate ligands in inorganic chemistry, and in organic catalysis.[9] On the other hand, aryl amines have been used very rarely as basic sites for the coordination of lanthanides.[10] The use of malonate functionalities with π-systems in direct conjugation with the two carbonyl moieties, to form π-extended ligands for metal cations, has not been, to the best of our knowledge, fully addressed.[11]

We report here on the supramolecular behaviour of a series of homologous molecular modules, in which crescent phenylenevinylene units are endcapped by identical dimethylamino and malonate groups. We show that the affinity of the ligand switches from the acceptor to the donor end in conjunction with both the hardness of the Lewis acid cation, and with the ''basicity'' of the binding sites on the ligands, which changes as a consequence of the elongation of the π-bridge (Fig. 1).

Results and discussion

Complexation response with lanthanides: UV studies

The comparison of the response induced by the binding event within the class of the three conjugated ligands 1–3 (Fig. 2) is presented.

The synthesis of the compounds has been previously reported.[12] We have set out to analyze, together with our previously used probe Eu^{3+},[8] the behaviour of Sc[3+], and other trivalent lanthanide ions, all as trifluoromethanesulfonate salts, since they are readily dissolved in MeCN. Sc[3+] has markedly different ionic radius and polarizability properties
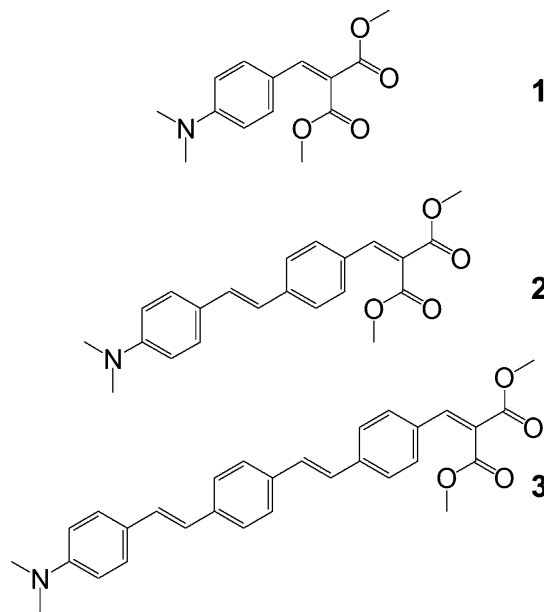

Fig. 2 Chemical structure of compounds 1–3.

with respect to lanthanides, yet it is often used for coordinating 1,3-dicarbonyl moieties as a lanthanide analogue,[9] and it can be used freely in ^{1}H NMR titrations as it is diamagnetic. Furthermore, we set out to use other lanthanides, such as Er[3+] and Yb[3+] possessing properties, such as their ionic radii, slightly different from Eu^{3+}.[13]

Chromophores 1–3 displayed intense absorption bands in the UV/Vis region. The absorption properties of 1–3 in MeCN solutions showed as expected a shift of the λ_{max} towards lower energies by the elongation of the π-conjugated bridge between the donor and the acceptor unit, but saturation seems to be reached readily, as there is not much further variations when going from compound 1 ($\lambda_{max} = 378$ nm) to compound 3 ($\lambda_{max} = 411$ nm in MeCN, entries 1, 6, 10 in Table 1). UV/Vis titrations were conducted in dry MeCN using the anhydrous triflate salts of Sc[3+], Eu^{3+}, Yb[3+] and Er[3+], and representative titrations are reported in Fig. 3 and in Fig. S1 and S2 (ESI†). In general, variations in the UV/Vis spectra were observed during all titrations, testifying for an effective interaction between the ligands (kept at a constant concentration, see Experimental) and the metal salts (which do not absorb in the spectral window examined).

The ICT red shift previously reported with 1 (in the presence of Eu^{3+}, titration b in Fig. 3, entry 3 in Table 1), however, cannot be generalized. In the case of Er[3+] and Yb[3+], the red shift is present, yet a very weak change in the absorption profile could be detected (Fig. S1, ESI,† titration g and h). The dramatic reduction in the intensity of the ICT upon complexation ($\varepsilon <$ 2000, Table 1, entries 4 and 5) cannot be ascribed to a major change in complexation geometry, since the maximum of this band is still located at 480 nm. This reduction has been previously observed in other complexes[8c] and linked to the overall geometry of the complex, which renders in these cases the spectroscopic transition formally forbidden by symmetry

Table 1 UV-Vis data (in MeCN) for ligands **1–3** and blue or red shift parameters upon complexation

Compound	λ_{max} (nm)	$\Delta\lambda_{max}$ (nm)	$\log K_a$ (M^{-1})
1	378 (27 500)[a]	—	—
1·Sc	269 (17 800)[a]	109[b]	4.5 ± 0.1 (2.4)[c]
1·Eu	474 (12 080)[a]	−96[b]	2.5 ± 0.1 (1)[c]
1·Er	477 (1200)[a]	−99[b]	2.6 ± 0.1 (1)[c]
1·Yb	481 (1900)[a]	−103[b]	2.5 ± 0.05 (1)[c]
2	406 (24 700)[a]	—	—
2·Sc	376 (22 800)[a]	30[b]	4.9 ± 0.1 (2.9)[c]
2·Eu	344 (26 600)[a]	62[b]	4.3 ± 0.15 (1)[c]
2·Er	345 (14 300)[a]	61[b]	4.8 ± 0.1 (1)[c]
3	411 (134 200)[a]	—	—
3·Sc	378 (171 300)[a]	33[b]	4.9 ± 0.1 (2.4)[c]
3·Eu	370 (236 200)[a]	41[b]	4.5 ± 0.2 (2.6)[c]
3·Er	382 (145 000)[a]	29[b]	4.3 ± 0.1 (0.9)[c]

[a] Numbers in parentheses refer to ε at the corresponding λ_{max}. [b] Difference between the λ_{max} of ICT of the free ligand and λ_{max} of the complex at saturation. A negative value indicates a red shift of the ICT band upon complexation, a positive value indicates a blue shift. [c] Numbers in parentheses refer to the coefficient obtained using the Hill equation. All nonlinear regressions for the best fit reported in Fig. 4 gave high confidence outputs ($r^2 > 0.995$).

consideration, and only weakly allowed by vibronic coupling. It is interesting to note that such huge variation is caused by a very minor change in the ionic radii of the cation.

In the presence of Sc^{3+}, certainly a "harder" Lewis acid than the previously mentioned ones, a blue shift occurs upon complexation with the same ligand **1** (titration a in Fig. 3). It is clear that a preferential change in the complexation site must take place, causing the switching from red to blue shifts. The coordination of Sc^{3+} to the nitrogen donor site as the preferred binding mode is not only intuitive, but also supported by ^{1}H NMR titrations (*vide infra*). This coordination event, effectively charging

the amine nitrogen atom, switches the dimethylamino site from being donor to acceptor, transforming the system from D−π−A to A−π−A and raising the HOMO–LUMO difference; thus the shift at higher energies (blue) of the ICT band.

The insertion of additional phenylenevinylene units, such as in compounds **2** and **3**, invariably produces blue-shifted complexes (the coordination to the nitrogen atom) upon coordination with either of Sc^{3+}, Eu^{3+}, and Er^{3+} (Fig. 3, titrations c–f and Fig. S1, ESI,† titrations i and l). In all these cases, therefore, the amine binding site prevails over the 1,3-dicarbonyl units as the preferred binding site for all metal cations tested independently of their relative "hardness" as Lewis acids.

The thermodynamic stability and the stoichiometry of the supramolecular complexes are examined next; the titration profiles at selected wavelengths are reported in Fig. 4. Even simple analyses indicate that the binding of the ligand and the metal cation in solution is not just 1:1. In the case of Sc^{3+} (titrations a, c and e) the sigmoidal profiles indicate the presence of multiple ligand–metal cation complexes, with various stoichiometric ratios; additionally, the sigmoidal shape of the titration profiles can indicate cooperative binding.[14]

The case of titration c, which exhibits an isosbestic point (confirmed by replicate titration at different concentrations, see Fig. S3, ESI†), is not straightforward to analyze.[14a] The stoichiometry cannot be 1:1, given the sigmoidal shape of the binding isotherm. Job plot analysis, carried out as reported by Sanders and Beeren[15] (Fig. S4a, ESI†), indicates a maximum at 0.55, which does not suggest a clear cut stoichiometry (4:3 is the ratio giving the closest value to that observed), but at least corroborates a binding mode other than 1:1. Compounds **2** and **3** have been shown to aggregate in CHCl$_3$ or DMF solutions of medium level concentrations,[12b] so that peculiar assemblies,
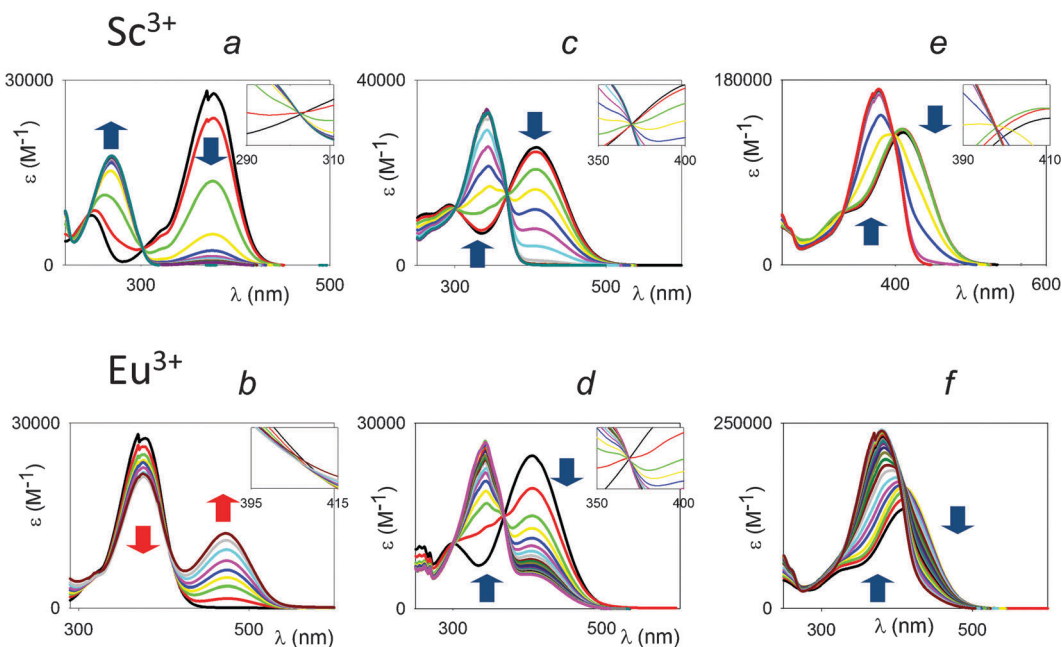

Fig. 3 UV/Vis titration experiments with Sc(OTf)$_3$ and Eu(OTf)$_3$ in MeCN for ligands **1** (left, a and b), **2** (center, c and d), **3** (right, e and f). Ligand concentrations were in the range: 1.1– 8.2 × 10^{-5} M.
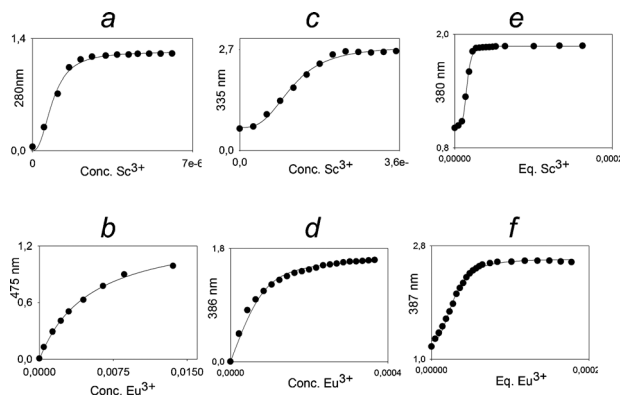
Fig. 4 Titration profiles (raw absorbance for given wavelength indicated on the y-axes) and best fit curves corresponding to the titrations shown in Fig. 3.

involving more than one ligand molecules stacked to each other in an antiparallel way, and coordinating metal cations through both nitrogen and carbonyl units, may help to rationalize the observed data.

In the case of the complexes with Eu^{3+}, the simplest ligand **1** (as previously reported,[10a] titration b in Fig. 4), but also **2** (titration d in Fig. 4) could be efficiently fitted using the equation derived for a 1:1 binding isotherm[16] (Table 1, Fig. S4b, ESI† for the Job plot). Apparent average binding constants between the host and the guest, obtained by application of the Hill equation,[17] confirmed that an increasingly extended π-bridge enhances the affinity between the ligands and the cation.

Sets of absorbance data shown in Fig. 3, for Sc(OTf)$_3$ and Eu(OTf)$_3$ titrated with **1–3**, were modelled using a factor analysis program called *Sivvu*, which takes into account *all* available wavelengths, and can potentially account for any set of equilibria.[18] Previous work with such analyses revealed that even data that appear to represent straightforward 1:1 binding exclusively may in fact evidence a plethora of supramolecular species.[8h] In this case, the analysis confirmed the complexity of the interpretation of the multiple species present in solution in most titrations (Tables S1–S6, ESI†). In particular, according to this analysis, when ligands **1–3** are titrated with Sc(OTf)$_3$, it appears that multiple complexes of the form ScL$_n$, n = 1,2,3, are formed. When ligands **1–3** are titrated with Eu(OTf)$_3$, there generally seems to be evidence for Eu$_2$L$_2$ and Eu$_2$L complexes.[19]

^{1}H NMR studies

The complexation properties were further investigated using ^{1}H NMR spectroscopy with Sc(OTf)$_3$ and, at low equivalent ratios, with Eu(OTf)$_3$. Shifts upon complexation were evident in both ligands **1** and **2** (Fig. 5 and 6).

For ligand **1** (Fig. 4 and Fig. S5, ESI†), the switch of the preferred binding site from the 1,3-dicarbonyl unit to the dimethylamino moiety, resulting in either a red or blue shift, by adding Eu^{3+} or Sc^{3+} (B and C respectively), is convincingly reinforced by the switch of the direction of the vinyl proton resonance shift upon complexation: 0.20 ppm downfield (from 7.60 to 7.80 ppm in the case of Sc^{3+}), and 0.15 ppm (7.60 to 7.45 ppm) upfield in the case of Eu^{3+}. The downfield shift is in
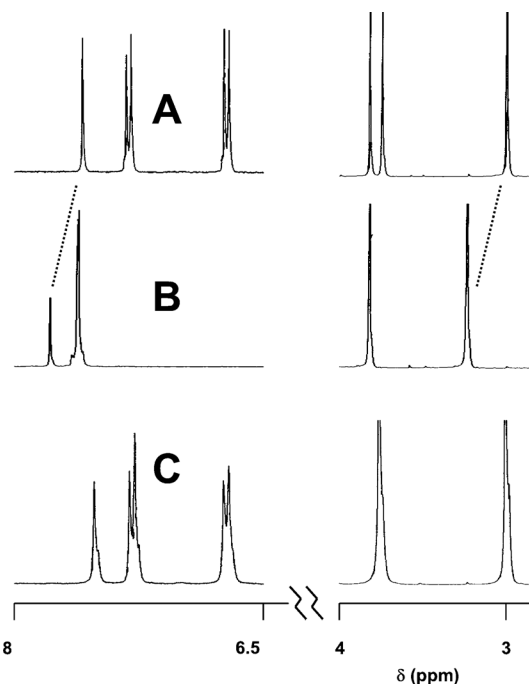

Fig. 5 ^{1}H NMR spectra (300 MHz) of: (A) ligand **1** (0.0126 M in CD$_3$CN); (B) **1** with 1.3 equivalents Sc(OTf)$_3$; (C) **1** with 0.2 equivalents Eu(OTf)$_3$.
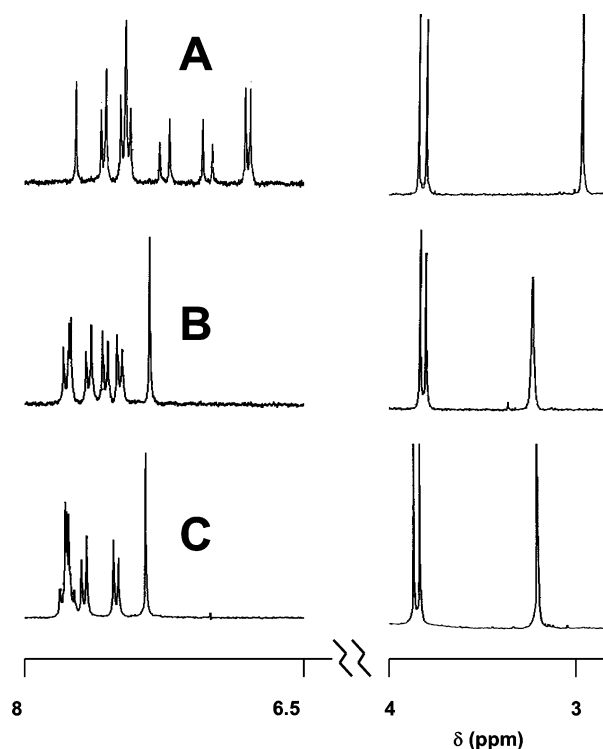

Fig. 6 ^{1}H NMR spectra of: (A) ligand **2** (0.007 M in CD$_3$CN); (B) **2** with 1.9 equivalents Sc(OTf)$_3$; (C) **2** with excess DCl.

agreement with a decreased electron density in the conjugated bridge caused by the coordination of the positively charged ion to the malonate acceptor end. In the case of Sc^{3+}, furthermore, the dimethylamino proton resonances shift about 0.25 ppm downfield

(from 3.00 to 3.25 ppm), and the aromatic protons collapse into a broad uncoupled singlet as typical of aromatic moieties directly linked to protonated ammonium ions.

The effect is similar in the case of ligand **2** (Fig. 6 and Fig. S6, ESI†); experiments were performed in this case only with Sc^{3+} (Fig. 6B). Again, the characteristic downfield shift of the dimethylamino protons can be observed. The singlet at *ca.* 7.3 ppm is due to the collapse of the aromatic proton resonances in proximity to the dimethylamino termini, as in the previous case. A further confirmation of the proposed model is given by the addition of DCl, protonating the nitrogen atom of the dimethylamino moiety (Fig. 6C): a proton chemical shift pattern superimposable to the previous one could be observed.

Molecular modeling studies

The different behaviour of ligands **1–3** in their supramolecular recognition of cations has been rationalized by analyzing the computed charge density distribution around their terminal dimethylamino and malonate ester functionalities. Geometry optimization of the three compounds has been performed at the PBE0/6-311++G(d,p) level *in vacuo* and in solution, considering both an apolar ($CHCl_3$) and a polar solvent (MeCN), in order to investigate the solvent effect on the charge distribution. The obtained wavefunctions have been submitted to topological analysis by using the Bader's Quantum Theory of Atoms in Molecules (QTAIM).[20] In Table 2 we report the dipole moments of compounds **1–3** and the QTAIM integrated net charges of the terminal moieties, as obtained by summing the integrated net atomic charges of the respective groups, *in vacuo*, in $CHCl_3$ and in MeCN. The charges obtained from the molecular electrostatic potential according to the CHelpG fitting scheme[21] are also reported in Table 2.

As already evidenced in our previous study on the ligands,[12b] the dipole moments of such push–pull molecules increase with an increase in the number of PPV units, though the variation is less than 2 Debye in solvent. By looking in more detail at the QTAIM charge distribution on the terminal groups, however, it

can be seen that the negative charge on the dimethylamino group increases along the series **1–3**, denoting a progressively reduced donor character of this group, while that on the malonate ester group decreases, indicating that it becomes a poorer acceptor site. Such a trend is more accentuated in solvent with respect to a *vacuum* and is particularly evident in acetonitrile, the solvent used in the experiments here reported. It is interesting to note that, in that solvent, the more negative terminus switches from the malonate group in **1** to the dimethylamino group in **2** and **3**, in agreement with the observed preference of the more extended compounds to coordinate the cations to the amine end with respect to the 1,3-dicarbonyl end. By looking at the CHelpG charges, the dimethylamino group is positively charged in **1** and becomes progressively less positive or even slightly negative when elongating the conjugated π-bridge, while the negative charge on the ester group systematically decreases in absolute values along the series **1–3**, with the only marginal exception obtained in chloroform on going from **2** to **3**. Therefore, both CHelpG and QTAIM approaches allow us to conclude that the D and A ends of the presently investigated compounds become progressively less good donor and acceptor groups, respectively, when increasing the length of the π-bridge, varying in this way their relative tendency to act as preferential coordinating sites.

Conclusions

We have reported on the supramolecular behaviour of a series of push–pull compounds, endcapped by functional groups with atoms bearing free lone pairs, acting as Lewis bases capable of recognizing cations such as lanthanide ions. The ligands exhibit striking differences in their supramolecular recognition of cations acting as Lewis acids. The shorter conjugated compound (one PPV unit) coordinates lanthanide cations (Eu^{3+}, Yb^{3+} and Er^{3+}) in MeCN solutions to the 1,3-dicarbonyl acceptor end, resulting in a red shift of the ICT band and thus in a supramolecular polarization of the system. By using the "hard" cation Sc^{3+}, recognition switches to the tertiary amine donor end, resulting in a blue shift of the ICT band and effectively changing the conjugated system from D–π–A to A–π–A. Upon enhancing the conjugation between the donor and the acceptor in the ligand, the coordination preference, regardless of the cation "hardness" (Sc^{3+}, Eu^{3+} and Er^{3+}), goes to the amine donor end. In terms of thermodynamic strengths and stoichiometries of the supramolecular complexes in solution, differences from case to case emerged, yet increasing values (from $\log K_{av} = 2.2$ to $\log K_{av} = 4.9$) are recorded with the increase of the π-conjugated bridge. As rationalized with the aid of molecular modelling studies, the switch of recognition of cations from the acceptor to the donor end as a consequence of the elongation of the conjugated π-bridge is to be ascribed to the relative variation in the charges of the two potential coordinating termini. In particular, it is found that, in MeCN, the more negative QTAIM net charge is on the 1,3-dicarbonyl end in the "shorter" ligand **1** of the series, while it switches on the dimethylamino end in the longer conjugated compounds **2** and **3**.

Table 2 Dipolar moments, μ (in Debye), and net charges, q (in e), on the dimethylamino and malonate groups in ligands **1–3** as obtained by QTAIM partitioning (first row) and CHelpG fitting scheme of the electrostatic potential (second row) *in vacuo*, in $CHCl_3$ and in MeCN[a]

		1	2	3
Vacuum	μ	4.89	6.53	7.20
	$q[N(CH_3)_2]$	−0.316	−0.323	−0.325
		0.003	*−0.038*	*−0.039*
	$q[C(COOMe)_2]$	−0.250	−0.214	−0.204
		−0.286	*−0.255*	*−0.250*
$CHCl_3$	μ	7.68	9.12	9.62
	$q[N(CH_3)_2]$	−0.282	−0.297	−0.301
		0.054	*0.013*	*−0.011*
	$q[C(COOMe)_2]$	−0.286	−0.240	−0.227
		−0.343	*−0.288*	*−0.291*
MeCN	μ	8.52	10.01	10.31
	$q[N(CH_3)_2]$	−0.270	−0.288	−0.294
		0.071	*0.032*	*0.002*
	$q[C(COOMe)_2]$	−0.302	−0.248	−0.234
		−0.349	*−0.299*	*−0.295*

[a] Wavefunctions obtained at the PBE0/6-311++G(d,p) level.

This study brings essential insights into tailorable organic chromophores for which, unexpectedly, small structural changes bring about opposite behaviour in terms of supramolecular behaviour and optical response. The results will be of great help in designing innovative conjugated sensors, and further efforts into a fine tuning of the molecular structures in order to match requirements for switchable optoelectronic applications can be foreseen.

Experimental

General methods

Compounds **1**–**3** [12b] were prepared as previously described. ^{1}H NMR spectra were recorded from solutions in CD_3CN on Bruker AMX300 with the solvent residual proton signal as a standard. Mass spectra were recorded using an Electrospray Ionization instrument.

General procedure for the titration experiments

The titration experiments were conducted as follows: to a stock solution of the ligand (solution A) in MeCN (UV/Vis spectroscopic grade) were added several aliquots of the guest (solution B). Solution B is formed by the lanthanide triflate at higher concentration dissolved in solution A, in order to maintain the ligand always at the same, constant concentration. In the case of a 1:1 binding isotherm, by employing a nonlinear fitting curve program, the plot of absorbance at a selected wavelength against the metal concentration was fitted by eqn (1), thus affording the value of the association constant K_a.

$$A = (\varepsilon_c - \varepsilon_s)\frac{k_a(C + x) + 1 - \left[[k_a(C + x) + 1]^2 - 4k_a^2 Cx\right]^{0.5}}{2k_a} + \varepsilon_s C$$

(1)

where A is the measured absorbance, x is the total concentration of the titrant added, ε_c is the molar absorptivity of the complex, ε_s is the molar absorptivity of the substrate at the desired wavelength, which could be directly determined, C is the total concentration of the ligand (which is a constant quantity), and K_a is the association constant for the 1:1 complex. [16]

The data for other titrations were fitted to a general form of the Hill equation:

$$\Delta Abs = \Delta Abs_{max} [x]^n K_a/(1 + [x]^n K_a)$$

which can be conveniently rewritten as:

$$\Delta Abs = \Delta Abs_{max} [x]^n/[(1/K_a)^n + [x]^n]$$

(2)

Eqn (2) could be fitted employing a nonlinear fitting program according to the general equation: $f(x) = a \times x^b/(c^b + x^b)$, obtaining values of $a = \Delta Abs_{max}$, $b = n$ (the Hill coefficient), $c = 1/K_a$. [17]

Job plot experiments

The Job plot experiments were conducted as follows: a solution of ligand **2** (76 μM, MeCN) was prepared, as was a solution of the triflate salt (76 μM, MeCN). The UV spectra of mixtures of the two solutions (at least ten) at different ligand:triflate salt ratios were then recorded. Plotting $\Delta A \times$ [ligand] against [ligand]/([ligand] + [cation]) produced the Job plot. [15]

Computational details

The molecular structures of ligands **1**, **2** and **3** have been optimized *in vacuo*, in $CHCl_3$ and in MeCN within the DFT approach, using the PBE0 functional. [22,23] The 6-311++G(d,p) basis set was chosen for all atoms. Solvent effects have been taken into account using the conductor-like polarizable continuum model, CPCM. [24] All calculations have been performed with the Gaussian suite of programs. [25] Topological analysis has been carried out with the AIMAll program. [26]

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