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Malonate Crown Ethers as Building Blocks for Novel D-π-A Chromophores

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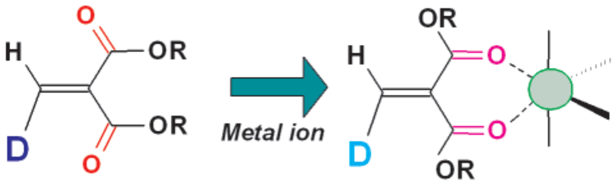
ABSTRACT

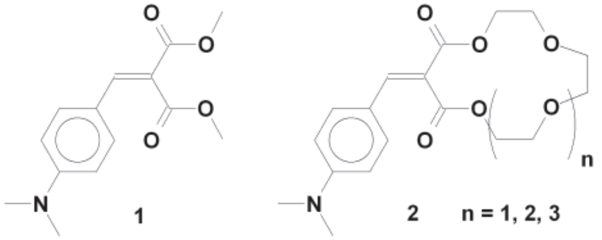


D = π-Electron Donating Group

A series of new crown ethers, incorporating a malonate ester functionality, have been synthesized and derivatized with π-electron rich aldehydes to give, conjugated, extended "push–pull" compounds. Their ability to bind Lewis acid-like metal cations, such as Mg^{2+} and Eu^{3+}, has been characterized, and the relative stability constants are presented. When the metal cation is bound to the malonate moiety within the crown ether cavity, the D-π-A character of the molecular structure is greatly enhanced.

"Push−pull" compounds, composed by a conjugated delocalized system in which one termini is electron-donating and the other is electron-withdrawing, are becoming increasingly popular for a series of material properties such as the design of second-order NLO organic materials.[1,2] In this context, organometallic systems are gaining attention because of several useful characteristics, such as, for example, the presence of a metal center able to undergo redox changes leading to enhanced molecular polarizabilities.[1c,3]

Malonate-containing crown ethers were synthesized and characterized in the late 1970s by Bradshaw and co-workers,[4] and later used as phase-transfer catalysts by others,[5] but their derivatization via manipulation of the malonate functionality has, to our knowledge, never been explored. It was recently reported that malonate compounds such as **1** or the corresponding crown ethers **2** are able to form weak complexes with Mg^{2+} salts in organic solvents (Figure 1). The complexation was inferred to involve directly the malonate moiety by both ^1H and ^{13}C NMR spectroscopic studies and also by an enhanced reactivity, in the presence of catalytic amount of the salt, of the exocyclic double bond in Diels−Alder reactions.[6]



1 **2** **n = 1, 2, 3**

Figure 1. Model compound **1** and malonate crown ethers **2a**−**c**.

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(1) (a) Burland, D. M.; Miller, R. D.; Walsh, C. A. *Chem. Rev.* **1994**, *94*, 31−75. (b) Kanis, D. R.; Marks, T. J.; Ratner, M. A. *Chem. Rev.* **1994**, *94*, 195−242. (c) Long, N. J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 21−28. (d) Marks, T. J.; Ratner, M. A. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 155−173.

(2) For a list of recent reports in the field, see: (a) Kenis, P. J. A.; Noordman, O. F. J.; Schönherr, H.; Kerver, E. G.; Snellink-Ruël, B. H. M.; van Hummel, G. J.; Harkema, S.; van der Vorst, C. P. J. M.; Hare, J.; Picken, S. J.; Engbersen, J. F. J.; van Hulst, N. F.; Vancso, G. J.; Reinhoudt, D. N. *Chem. Eur. J.* **1998**, *7*, 1225−1234. (b) Alain, V.; Blanchard-Desce, M.; Ledoux-Rak, I.; Zyss, J. *Chem. Commun.* **2000**, 353−354. (c) Lin, W.; Ma, L.; Evans, O. R. *Chem. Commun.* **2000**, 2263−2264. (d) Moore, A. J.; Chesney, A.; Bryce, M. R.; Batsanov, A. S.; Kelly, J. F.; Howard, J. A. K.; Perepichka, I. F.; Perepichka, D. F.; Meshulam, G.; Berkovic, G.; Kotler, Z.; Mazor, R.; Khodorkovsky, V. *Eur. J. Org. Chem.* **2001**, 2671−2687. (e) Gangopadhyay, P.; Radhakrishnan, T. P. *Angew. Chem., Int. Ed.* **2001**, *40*, 2451−2455. (f) Aqad, E.; Leriche, P.; Mabon, G.; Gorgues, A.; Khodorovsky, V. *Org. Lett.* **2001**, *3*, 2329−2332.

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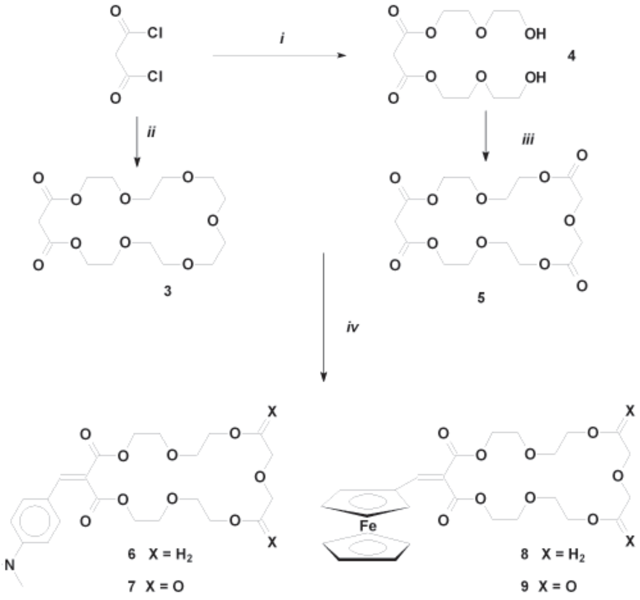
Since these compounds are composed of a π-electron-donating aromatic unit and an electron-withdrawing group (the malonate ester functionality) which could be further polarized by the coordination of a metal cation, we set out to investigate the possibility of assembling more stable complexes between crown ethers containing a malonate moiety and selected Lewis acid metal cations in order to ascertain possible future applications as D-π-A chromophores in functional devices.

Crown ether **3** was obtained in good yields (40%) by the macrocyclization reaction of malonyl dichloride and hexaethylene glycol in high dilution conditions.[7] We also pursued the introduction of further "soft" carbonyl functionalities while preserving the overall dimension of the crown ether structure at 22 atoms. Reaction of malonyl dichloride (Scheme 1) with diethylene glycol monobenzyl ether, and subsequent deprotection by hydrogenolysis, afforded compound **4** in good yields, and high dilution cyclization with diglycolyl dichloride afforded crown ether **5** in good yields (25%).

Scheme 1[a]



[a] Reagents and conditions: (i) diethylene glycol monobenzyl ether, PhH, Δ, then H_2, 10% Pd/C, EtOH, rt; (ii) hexaethylene glycol, PhH, Δ; (iii) diglycolyl dichloride, PhH, Δ; (iv) 4-dimethylaminobenzaldehyde or ferrocenecarboxaldehyde, piperidinium acetate, PhH, Δ.

Functionalization of the malonate moiety via Knoevenagel condensation was carried out with piperidinium acetate as a catalyst, either with 4-dimethylaminobenzaldehyde or ferrocenecarboxaldehyde. Purification by column chromatography afforded compounds **6**−**9** in 70−90% yield as orange (**6**, **7**) or deep red (**8**, **9**) compounds. The UV−vis spectra of these compounds showed an intramolecular charge-transfer band (ICT) as direct evidence of their extended, dipolar nature, centered at 380 nm for compounds **6** and **7**, and at 480 nm for compounds **8** and **9** (see also Figure 2).

Upon addition of Mg^{2+} as a chelating metal cation into MeCN solutions of **1** or **7**, the ICT (centered at 380 nm) is drastically shifted (ca. 100 nm), indicating an additional polarization of the system upon coordination of the metal cation to the 1,3-dicarbonyl system.[8] Albeit we explored the qualitative behavior of other salts (such as Co(II), Cu(II), and Fe(II) salts), which proved to be similar in terms of UV/vis spectroscopic behavior, we set out to determine the thermodynamic stability constants between the above-mentioned crown ethers and magnesium perchlorate (MP) and europium triflate (ET), since these salts have good solubility in MeCN and their cations represent two opposites in terms of ionic radii and polarizability.[9]

The stability constants of the ligand−metal complexes could be evaluated in MeCN at 25 °C by means of UV/vis spectrophotometric titrations. Isosbestic points were found in all titrations, strongly indicating the presence of a unique complex in solution.[10]

Two examples of such titrations are shown in Figure 2. The values for the stability constants, together with the observed λ_{max} for the ICT band associated with the forming complexes, are reported in Table 1. In the case of Mg(ClO_4),[11] binding with model compound **1** was clearly detectable but too weak to be determined with sufficient precision ($\log k_a < 1$). A similar experiment between **1** and ET revealed instead a much stronger binding (see Table 1, entry 1).[12]

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(3) For selected recent examples, see: (a) Barlow, S.; Marder, S. R. *Chem. Commun.* **2000**, 1555−1562. (b) Jayaprakash, K. N.; Ray, P. C.; Matsuoka, I.; Bhadbhade, M. M.; Puranik, V. G.; Das, P. K.; Nishihara, H.; Sarkar, A. *Organometallics* **1999**, *18*, 3851−3858. (c) Müller, T. J. J.; Netz, A.; Ansorge, M.; Schmälzlin, E.; Bräuchle, C.; Meerholz, K. *Organometallics* **1999**, *18*, 5066−5074. (d) Di Bella, S.; Fragalà, I.; Ledoux, I.; Zyss, J. *Chem. Eur. J.* **2001**, *7*, 3738−3743.

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(8) Coordination of the metal cation to the 1,3-dicarbonyl system is further substantiated by ^{13}C NMR studies of crown ether **7** in the presence of increasing amounts of magnesium perchlorate or of europium triflate in d_3-MeCN, similarly to what reported in ref 6.

(9) For determination of stability constants between 18-crown-6 and lanthanide salts, see: (a) Bünzli, J.-C.; Wessner, D. *Helv. Chim. Acta* **1981**, *64*, 582−596. (b) Bünzli, J.-C.; Pilloud, F. *Inorg. Chem.* **1989**, *28*, 2638−2642. (c) Piguet, C.; Bünzli, J.-C. *Chem. Soc. Rev.* **1999**, *28*, 347−358. See also: Izatt, R. M.; Pawlak, K.; Bradshaw, J. S.; Brueniong, R. L. *Chem. Rev.* **1991**, *91*, 1721−2085.

(10) Connors, K. A. *Binding Constants*; Wiley: New York, 1987.

(11) The possibility of using magnesium triflate was prevented by its almost total insolubility in MeCN.

(12) Titration experiments were usually conducted adding increasing amounts of metal salt to a solution at costant concentration of crown ether. In the case of ligand **1**, a titration was also conducted adding increasing amounts of ligand **1** to a solution at costant concentration of ET, obtaining essentially identical results in the calculation of the association constant.

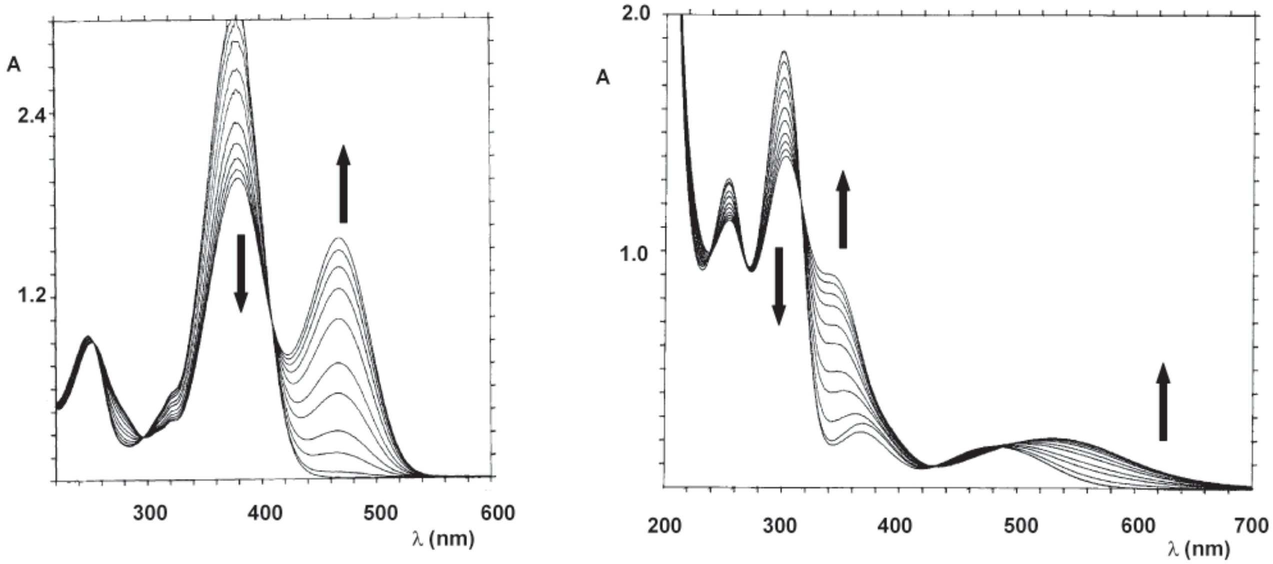

Figure 2. UV/vis spectrophotometric titrations between compound **7** and Mg(ClO_4)$_2$ (left) and compound **9** and Eu(OTf)$_3$ (right).

A Job plot experiment[10] between **1** and Eu(OTf)$_3$ in MeCN at 25 °C revealed a 1:1 stoichiometry, and a similar experiment also confirmed a 1:1 stoichiometry for the complex between **7** and ET, suggesting that the three triflate counterions are directly involved in the coordination sphere of the metal cation and are therefore able to statisfy the high coordination number of Eu^{3+}.[13] Mass spectrometric analysis of two solutions containing different ratios between **7** and ET (1.5:1 and 1:3 of **7**:ET in MeCN) showed that also in the gas phase the 1:1 stoichiometry is the preferred one, as revealed by the peak at 960 *m*/*z*, corresponding to the 1:1 complex with the loss of the triflate counterion (Figure 3).

The results displayed in Table 1 show how crown ethers **6** and **7** do form more stable complexes (ca. 1 order of magnitude) with ET than the corresponding, D-π-A open ligand **1** (entries 3 and 5 vs 1 in Table 1). There is also a marked selectivity in the binding of ET vs MP.

Table 1. Association Constants between Compounds **1** and **6**−**9** and Europium Triflate (ET) and Magnesium Perchlorate (MP) in MeCN at 25 °C[a]

entry	ligand	log k_a	λ_{max} (nm)[b]
1	**1**	2.60 ± 0.05 (ET)[c]	478
2	**6**	2.0 ± 0.2 (MP)[c]	430
3	**6**	3.9 ± 0.1 (ET)[c]	450
4	**7**	1.2 ± 0.05 (MP)[c]	466
5	**7**	3.8 ± 0.1 (ET)[c]	476
6	**8**	3.5 ± 0.1 (ET)[c]	530
7	**9**	3.2 ± 0.1 (ET)[c]	530

[a] All values for the stability constants are in M^{-1}. The values reported are the average of at least two independent titrations, with all nonlinear regression giving high confidence outputs ($r^2 > 0.995$). [b] Maximum for the ICT band related to the metal cation:ligand complex. [c] MP indicates a value obtained by titration with magnesium perchlorate, whereas ET indicates a value obtained by titration with europium triflate.

In the case of ferrocene-derived compounds **8** and **9**, the ICT upon complexation undergo a more limited bathocromic shift (ca. 50 nm). The association constants with ET also do show a somewhat reduced stability when compared with **6** and **7**, probably as a consequence of both steric and electronic effects related to the different substituents. The maximum of the ICT band upon complexation (530 nm) is well above that of compounds **6** and **7**, suggesting higher NLO responses for these compounds.[1c]

The introduction of further carbonyl functionalities (**7** and **9** vs **6** and **8**) do not seem to bring any additional stabilization. There are, however, substantial differences regarding the maximum wavelength for the ICT of the 1:1 complex, both in the case of ET and MP. Whereas with crown ether **7** the above-mentioned values are very close to

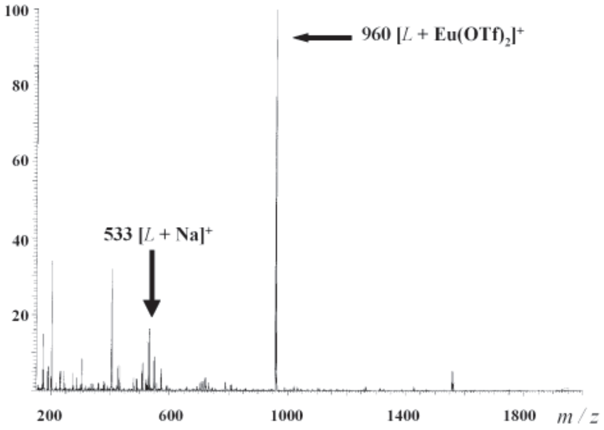

Figure 3. Mass spectrum (ESI) of a 1:3 solution of crown ether **7**:ET in MeCN.

those recorded with model compound **1**, in the case of **6** these values are somewhat distant. We speculate this is an indication of a more or less optimal interaction with the 1,3-dicarbonyl chromphore moiety by the metal cation, probably as a result of subtle differences in complexation geometry.[14]

In conclusion, we have synthesized and characterized novel functionalized, "push−pull" crown ethers which are able to form thermodinamically stable 1:1 complexes with ET in MeCN solutions. Their structures are however crucial in order to obtain and maximize interaction between the metal cation and the cromophore moieties of the compounds.

We are currently evaluating the NLO responses of these complexes and, given the noteworthy absorption/emission properties of lanthanides, their possible utilization as light harvesting or energy converting devices.[15]

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Supporting Information Available: Full experimental procedures for compounds **5**−**9**, together with detailed experimental procedure for the determination of the binding constants and selected examples of titration curves. This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) Albeit compound **7** is crystalline, all attempts to grow good quality single crystals of the complex with ET failed.

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