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Rotamerism-Driven Large Magnitude Host-Guest Binding Change in a Crown Ether Derivatized Pyridinium-Phenolate Series

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Two TICTOID-based pyridinium-phenolates bearing a crown ether macrocycle have been designed for the complexation of potassium cation. The nucleophilicity of the intraannular phenolate O^- function can be strongly modulated by biaryl twisting. Such a structure/electronic transduction effect gives rise to a host-guest binding change by more than two orders of magnitude.

Since recent decades, one of the smallest merocyanine dye, namely the 4,4'-N-methylpyridinium phenolate, has become the molecular prototype for the design algorithm of new generations of TICTOID-based¹⁻⁶ chromophores exhibiting some of the largest nonlinear responses ever identified^{5, 6}. Whereas the *well-established* design principles⁷⁻⁹ to improve the NLO performances of π -conjugated D-A chromophores aim to tune the degree of bond length alternation (BLA) by increasing dimensionality, planarity or D/A strength of the end capping substituents, the TICTOID strategy alternatively proposes to re-focus into smaller D-A molecules and to enforce the zwitterionic character of their ground state by increasing the inter-aryl twist angle (Θ in **Scheme 1**).

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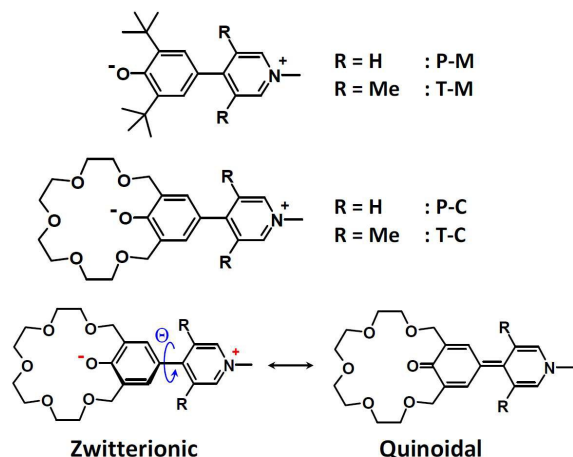
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Such an electronic decoupling between the donor and acceptor π -subfragments leads to a charge separation which induces an extremely large polarization in the system with subsequent unprecedentedly large NLO properties^{5, 6}. One interesting ramification of this fundamental structure/property relationship is to modulate the nucleophilicity of the aryl O^- group as a function of Θ when using pyridinium-phenolate as TICTOID prototype. Such a very promising property correlated to the rotamerism effect can be implemented into a judiciously designed chromoionophoric architecture in which the TICTOID module participates to the ion coordination. By this way, one should expect a modulation of the host-guest binding ability driven by Θ . In line with this ground premise, we have designed two crown ether modified pyridinium-phenolate derivatives (**P-** and **T-C** in **Scheme 1**) in which: *i*) The macrocyclic polyether substituent is grafted on the phenolate moiety in such manner that the intraannular aryl O^- group exhibit an efficient anchoring effect during the cation coordination¹⁰. *ii*) This receptor has previously demonstrated an adequate selectivity against $\text{K}^{+11, 12}$ due to the size of the crown-ether-mediated complexation combined with an efficient ion/dipole interaction with the central phenolate. *iii*) The dihedral twisting within biaryl dyes is induced by steric crowding of methyl substituents on the pyridinium core and located in ortho position to the inter-aryl central bond. It is noteworthy that this latter substitution effect induces a Θ -change ranging from 10° to 45° as previously calculated for model compounds¹³ **P-** and **T-M** (**Scheme 1**). We will see however that this apparently weak rotamerism effect have a striking incidence with respect to the host-guest binding ability.

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Scheme 1. Molecular structures of the chromophores. Zwitterionic and quinoidal forms of crown ether derivatives.

In order to evaluate the weighted contribution of the zwitterionic form in ground state, we will first compare the electronic and spectroscopic properties of the crown ether systems in regard with their respective model chromophores. **Figure 1** depicts the absorption spectra of each compound in acetonitrile and **Table 1** summarizes the related spectroscopic data. The high energy region of the spectra displays distinctive absorption bands which mainly correspond to electronic transitions centred on each phenylene fragment. According to the 'intensity-borrowing' mechanism¹⁴⁻¹⁶, the planarization of the biaryl systems leads to a significant decrease of these bands to the benefit to the longest wavelength absorption band which corresponds to the inter-subfragment charge transfer (CT) excitation.

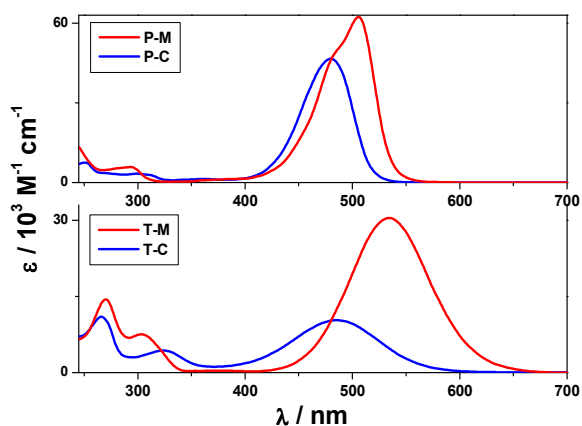


Fig.1 Absorption spectra of the phenolate derivatives in acetonitrile (2×10^{-3} M of tetramethylguanidine used as a base).

	λ_{abs} / nm	ϵ / $M^{-1}cm^{-1}$	E_g^a / eV	M_{abs}^b / D	δ^c / ppm	E^d / V vs. SCE E_{red} E_{ox}	pK_a^e
P-M	506	62000	2.32	8.2	180.8	-1.83 0.37 ^r	9.1
P-C	477	46600	2.40	7.0	176.6	-1.70 0.65	8.3
T-M	534	30500	2.04	6.6	172.7	-1.78 0.13 ^r	12.0
T-C	485	10300	2.20	4.2	167.2	-1.69 0.36	10.9

^a HOMO-LUMO optical gap measured from the onset of the CT band. ^b Calculated from ref. 16. ^c ¹³C NMR chemical shift¹⁸ in CD₃OD. ^d solvent: ACN ^e in ACN/Water (1v/1v). ^r reversible

Table 1. Summary of spectroscopic and electrochemical data in acetonitrile. pK_a values of chromophores in aqueous medium.

It should be noted that this CT band is more blue-shifted for the crown ether dyes as compared to their respective model derivatives. Such a hypsochromic effect has been previously observed for a similar crown ether E_T(30)-betaine dye^{11, 12, 17} and should be mainly attributed to a less efficient solvation of the phenolate O⁻ group which is surrounded by a polyether chain. For each chromophore, the calculated values for the transition dipole moment of the CT band (M_{obs}) are reported in **Table 1**. This parameter which evaluates the allowed character of the CT transition constitutes the relevant criterion to quantify the degree of electronic conjugation between phenolate and pyridinium subunits¹⁶. It is interesting to note that M_{obs} clearly undergoes a gradual decrease following the order **P-M**, **P-C**, **T-M** and **T-C**. This tendency suggests that the combination of structural changes such as inter-aryl twisting and, in less extent, crown ether derivatization converges to an effective electronic decoupling between pyridinium and phenolate moieties. The subsequent zwitterionic charge localization in ground state is also corroborated by a clear upfield displacement of the ¹³C NMR chemical shift related to the carbon adjacent to the phenolate O⁻ function (δ in **Table 1**). As shown in **Figure 2**, the gradual decrease of M_{obs} correlates well ($R^2 \sim 0.949$) that observed for δ which nicely confirms that the sterically induced electronic decoupling of the donor and acceptor π -subfragments induces the increase of the nucleophilicity of the aryl O⁻ group. As a consequence, the basicity of the phenolate group should be enhanced which is confirmed by a significant increase of the pK_a value of about 2.6 units from **P-C** to **T-C** (see **Table 1**)

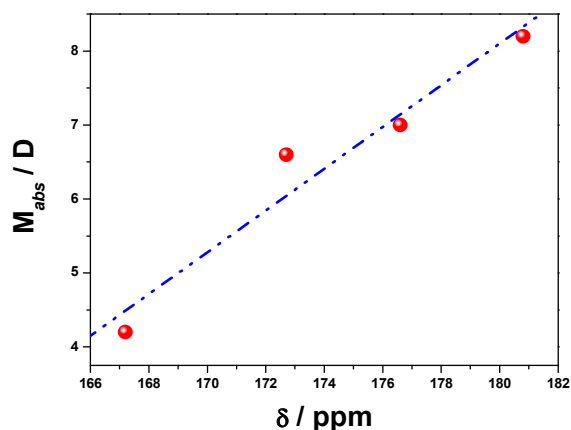


Fig.2 Correlation between CT transition dipole moments and ^{13}C NMR chemical shifts¹⁸ relative to the carbon atom bearing the phenolate oxygen.

The charge-richness on the phenolate group can be also evaluated by comparison of the oxidation properties of the chromophores. The values of redox potentials measured by cyclic voltammetry in acetonitrile are gathered in **Table 1** and the corresponding cyclic voltammograms (CVs) are depicted in **Figure S1**. Firstly, the HOMO-LUMO (electrochemical) gaps estimated from the oxidation and reduction potentials reasonably agree with the optical ones. Secondly, one can clearly observe that the oxidation potential is very sensitive to rotamerism effects. The model compounds both exhibit one chemically reversible oxidation wave which shifts to the low potentials (ΔE_{ox} : -0.24 V) with the increase of Θ (see **Figure S1**, ESI). Despite a loss of reversibility in their CVs, the same tendency can be observed for the crown ether derivatives with a significant ΔE_{ox} of about -0.29 V on going from **P-C** to **T-C**. Hence, the twisted pyridinium-phenolate compounds clearly present a better oxidizing ability than their planar homologues which corroborates the enhancement of the negative charge density on the phenolate subunit. Such a charge localization effect will presumably promote a strong ion-dipole interaction upon complexation reaction between potassium cation and **T-C** as will be highlighted hereafter.

Figure 3 shows the evolution of the absorption spectra of crown ether systems in acetonitrile in presence of increasing amount of K^+ . The coordination of the cation to the donor part of the D-A chromoionophores clearly induces a hypsochromic shift of the CT band which should be ascribed to the electrostatic O^- / K^+ interaction leading to an increase of the ionization energy of the phenolate subunit. This assumption is also corroborated by the fact that the oxidation potential of the each ligand clearly shifts

to higher potentials in presence of an excess of potassium salt (see **Figure S2**). Note that, in the same conditions, the absorption CT band of the model compounds is hardly sensitive to the presence of the cation. This obviously underlines the mediating role of the crown ether chain in the complexation reaction.

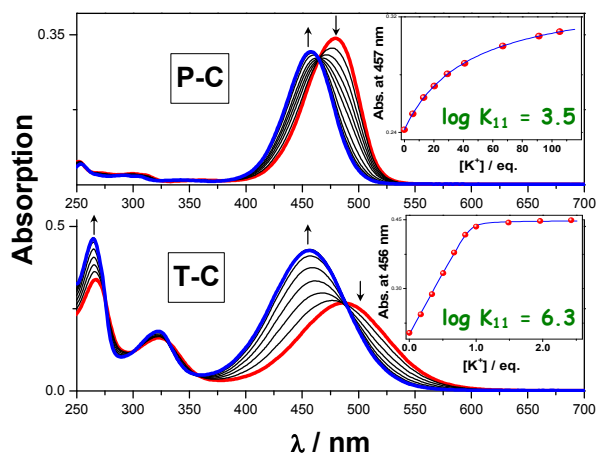


Fig.3 Changes of the absorption spectra of crown ether derivatives with increasing concentration of K^+ in acetonitrile (2×10^{-3} M of TMG used as a base). Insets: titration curves (circles) + best-fitting curves (line). [**P-C**] = 7.3×10^{-6} M and [**T-C**] = 2.5×10^{-5} M.

The absorption changes as function of K^+ concentration were analyzed with the assumption of a 1:1 stoichiometry and the related binding constants (K_{11}) were calculated according to the formalism proposed by Valeur *et al.*¹⁹. The insets in **Figure 3** show the best-fitting curves to the experimental data using least squares analysis. The most striking result resides in the high binding constant of **T-C** with a value of ca. 6.3 ± 0.3 in logarithmic scale. This very strong complexation ability clearly contrasts with that observed for **P-C** which exhibits a much lower binding constant with a value of ca. 3.5 ± 0.1 (in log. scale). Hence, we demonstrated that the charge localization driven by rotamerism effects leads to a large range host-guest binding change with a complexation constant increasing by more than two orders of magnitude on going from the planar to the twisted chromoionophore.

In summary, we have designed two novel TICTOID-inspired chromoionophores in which the weighted contribution of the charge-separated zwitterionic form in ground state can be modulated by the interaryl twist dihedral angle. Such a twisting strategy leads to a clear enhancement of the nucleophilicity on the phenolate oxygen. This latter 'transducing function' has been

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strategically positioned in such manner that it also plays a key anchoring role within the cation coordination sphere. As a consequence, we successfully demonstrated a large magnitude 'host-guest' binding change by a simple relaxation of this twist angle coordinate. It is clear that such a relevant structure/property relationship paves the way for the design of more sophisticated phenolate-pyridinium ionophore in which an irreversible photoinduced cascade reaction induces the interaryl twisting relaxation. Hence, potential applications related to the photoinduced disruption of the 'host-guest' interaction and subsequent release of species in the medium should emerge from this very promising property.

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