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First representatives of functionalized D–π–A chromophores containing a tunable hydroxytricyanopyrrole (HTCP) acceptor and *N*,*N*-disubstituted aminophenyl donor†

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The first representatives of D–π–A chromophores containing a hydroxytricyanopyrrole (HTCP) acceptor and *N*,*N*-disubstituted aminophenyl donor were synthesized. The obtained molecules include reactive NH- and OH-fragments allowing the photophysical properties of the chromophores to be tuned, which is not possible for the well-known chromophores of the tricyanofuran (TCF) and tricyanopyrrole (TCP) series. The absorption properties of the synthesized HTCP-chromophores with a *p*-aminophenyl electron donor substituent were thoroughly studied.

Donor–acceptor chromophores containing tricyanofuran (**TCF**) or tricyanopyrrole (**TCP**) acceptors are widely used in the development of solar cells,[1–5] electro-optic,[6–8] photochromic,[9–11] non-linear optic[12–17] and solid-state fluorescent[18–20] materials as well as luminescent labels and probes.[21–25] Promising physicochemical and optical properties have been reported for the conjugated D–π–A compounds bearing a substituted amino group as a donor. Molecules with the electron donating *p*-aminophenyl fragment and nitrile-rich pyrrole or furan ring as an acceptor are examples of these chromophores (Fig. 1).

4-Aminophenyl-**TCF** derivatives (more than 40 examples have been described) and compounds of the 4-aminophenyl-**TCP** series (more than 100 examples have been described) can be used as fluorescent probes for the analysis of proteins and visualization of cells and tissues.[26–31] They are also known as chromophores for electro-optical polymer devices,[32,33] as nonlinear optical chromophores for biomedical imaging,[34] as dyes for printing[35] and as pigments to dye synthetic textile materials.[36–38] These compounds are promising for photoelectric conversion elements and semiconductor electrodes[39] as well as for the direct visualization of mechanical contacts using fluorescence microscopy.[40]

In previous work, hydroxytricyanopyrrole (**HTCP**) which was obtained from an α-diketone and malononitrile dimer (DMN) was reported as a more functionalized analogue of **TCF** and **TCP** acceptors.[41,42] This compound is still not well studied and is characterized by the presence of functional groups, which can be easily modified. This property expands the possibility for the synthesis of molecules with given optical and electrochemical properties.

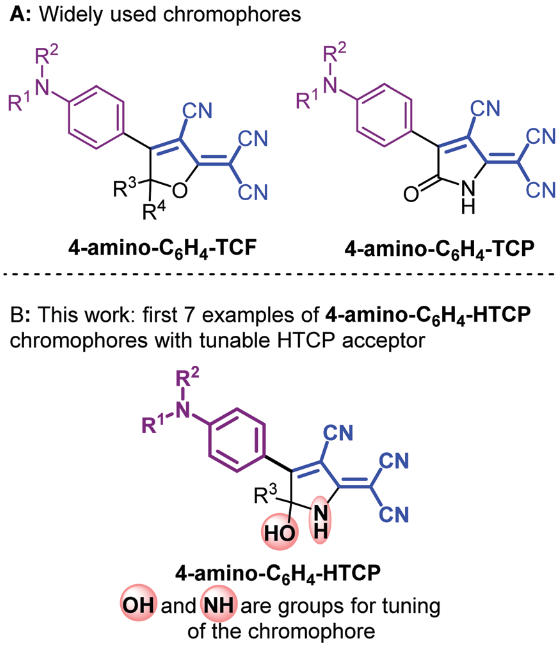

Fig. 1 Known **TCF** and **TCP** and herein studied **HTCP** chromophores with a *p*-aminophenyl donor.

The reported approach of **HTCP** synthesis[41,42] allows an electron-donating moiety to be introduced in the fourth position of the pyrrole ring by choosing a starting ketone with a necessary substituent. It should be noted that about 15 examples of **HTCP** derivatives have already been described,[43–46] however, there was no mention about **HTCP** chromophores with a *p*-aminophenyl substituent in the fourth position of the pyrrole ring.

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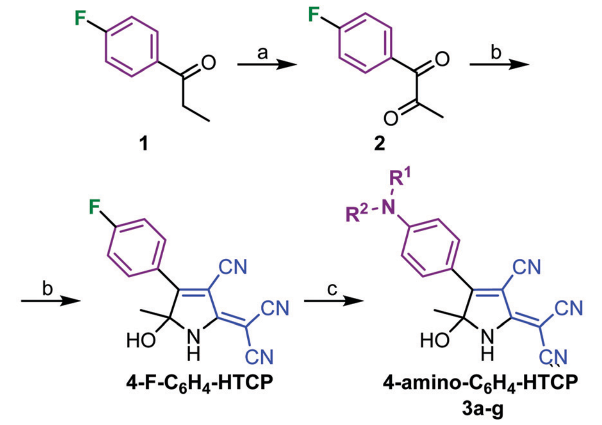
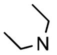
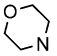
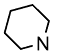
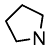
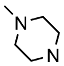
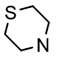
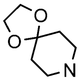
Table 1 Synthesis of compounds **3a–g**



(a) SeO_2, 1,4-dioxane, H_2O, reflux, 6 h, 68%; (b) malononitrile dimer, $AcONH_4$, EtOH (80% aq.), 0°C, 48 h, 71%; (c) R^1R^2NH, pyridine, rt, 24-72 h, 52-84%.

Product	R^1R^2N	Yield[a] (%)
3a		52
3b		68
3c		84
3d		57
3e		66
3f		78
3g		59

[a] Yield of the isolated product.

Thus, the aim of this work was to synthesize the first representatives of **HTCP**-based donor–acceptor chromophores with the *p*-aminophenyl substituent as a donor in the fourth position of the pyrrole ring and to investigate their optical and electrochemical properties.

Firstly, we directly synthesized **4-F-C_6H_4-HTCP** by expanding our previously developed procedure upon 1-(4-fluorophenyl)-propane-1,2-dione **2** and malononitrile dimer (DMN) (Table 1) for the further synthesis of **4-amino-C_6H_4-HTCP 3**.[14] The starting α-diketone **2** was obtained by an oxidation of 1-(4-fluorophenyl) propan-1-one **1** with selenium dioxide. The presence of a fluorine atom in **4-F-C_6H_4-HTCP** allows a nucleophilic substitution reaction to be used for introducing an amino moiety into the molecule. We found that the reaction of **4-F-C_6H_4-HTCP** with amines occurs in a pyridine medium at room temperature for 24–48 h and results in the formation of the desired 2-(3-cyano-5-hydroxy-5-methyl-4-(4-aminophenyl)-1,5-dihydro-2*H*-pyrrol-2-ylidene)malononitriles **3a–g** in 52–84% yield.

The structure of compounds **4-F-C_6H_4-HTCP** and **3a–g** was supported by the data of ^{1}H and ^{13}C NMR and IR spectroscopy, mass spectrometry and elemental analysis. IR spectra of the synthesized compounds are characterized with the absorption bands of the hydroxyl group and NH-fragment (3368–3189 cm^{-1}) and conjugated cyano groups (intensive bands at 2221–2196 cm^{-1}). ^{1}H NMR spectra of compounds **4-F-C_6H_4-HTCP 3** contain a pyrrolic NH proton signal at 10.78 ppm, *o*- and *m*-aryl protons at 8.10–8.14 and 7.48–7.53 respectively, the broadened signal of hydroxyl protons at 7.37 ppm and protons of the methyl group around 1.49 ppm. The ^{13}C NMR spectra of compounds **4-F-C_6H_4-HTCP** exhibit downfield shifted signals of C-atoms of the second and fourth positions of the pyrrole cycle at 170.16 and 160.17 ppm respectively and the signals of C-atoms of the third and the fifth position of the pyrrole ring at 101.51 and 94.47 ppm. A characteristic of the ^{13}C NMR spectra is the appearance of signals of three cyano groups at 114.96–112.39 ppm and of weak intense signals of C-atoms of $C(CN)_2$ fragments at 45.28 ppm. The presence of fluorine in the molecule causes the spin–spin coupling of the aromatic carbon atoms and the corresponding signals appear as doublets at 164.37, 131.50, 124.90 and 116.50 ppm. ^{1}H and ^{13}C NMR spectra of compounds **3a–g** differ in the presence of signals of the corresponding atoms of the introduced *N*,*N*-disubstituted amino moiety at 1.15–3.75 ppm for the ^{1}H NMR spectra and at 12.50–65.80 ppm for the ^{13}C NMR spectra. The mass spectra are characterized by the presence of peaks of molecular ions $[M]^+$ with 2–17% intensity (EI, 70 eV).

In the next stage of our work, we studied the photophysical properties of compounds **3a–g**. It was found that the absorption spectra of compounds **3a–g** in acetonitrile have an absorption maximum in the visible part of the spectrum in the range of 448–476 nm (Fig. 2) and are characterized by the logarithms of extinction coefficients from 4.49 to 4.78 (Table 2). For compounds **3a, c and d** with alkyl and carbocyclic substituents at the amino nitrogen atom, the absorption maximum lies in the longer wavelength range of the spectrum (470–476 nm). For compounds **3b and e–g** containing other heteroatoms in the substituent, a hypsochromic shift of the absorption spectral band is observed.

It is known that compounds of the **TCF** and **TCP** series can be used as sensitizers of solar cells, as well as in other electro-optical

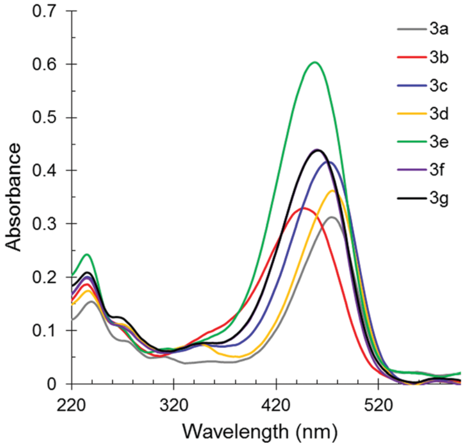


Fig. 2 Absorption spectra of compounds **3a–g** in acetonitrile (C = 1.0×10^{-5} M).

Table 2 Electrochemical characteristics of compounds **3a–g**

				HOMO (eV)		E_g (eV)		LUMO (eV)	
Comp.	$E_{\text{ox}}^{\text{onset}}$ *vs.* Ag/AgCl (eV)	$\lambda_{\text{abs}}^{\text{onset}}/\lambda_{\text{abs}}^{\text{max}}$ (nm)	$\log\varepsilon$	Found	Calc.	Found	Calc.	Found	Calc.
3a	0.45	520/474	4.49	−4.85	−5.81	2.39	2.89	−2.46	−2.91
3b	0.71	513/448	4.52	−5.11	−5.92	2.42	2.95	−2.69	−2.97
3c	0.94	525/470	4.62	−5.34	−5.77	2.37	2.86	−2.97	−2.91
3d	0.51	523/476	4.56	−4.91	−5.78	2.37	2.89	−2.54	−2.89
3e	0.67	519/458	4.78	−5.07	−5.87	2.39	2.92	−2.68	−2.95
3f	0.69	515/460	4.64	−5.09	−5.84	2.41	2.89	−2.68	−2.95
3g	0.77	514/460	4.64	−5.17	−5.81	2.42	2.90	−2.75	−2.91

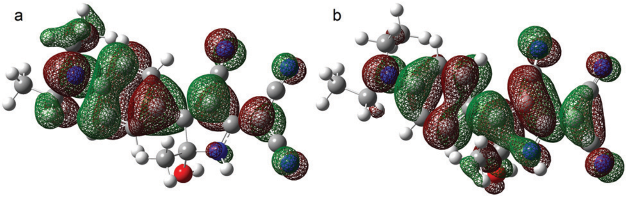


Fig. 3 Visualized HOMO (a) and LUMO (b) orbitals of compound **3a**.

or nonlinear optical materials.[8,9,12] To evaluate the possibility of using the synthesized 2-(3-cyano-5-hydroxy-5-methyl-4-(4-aminophenyl)-1,5-dihydro-2*H*-pyrrol-2-ylidene)malononitriles **3a–g** in these fields we estimated their HOMO and LUMO energy levels (Fig. 3).

All calculations were carried out in the Gaussian 09 programming package at the DFT level of theory. Becke's three parameter (B3) gradient-corrected exchange functional combined with the Lee–Yang–Parr (LYP) correlation functional and 6-31G+g(d,p) basis set was utilized.

As it is visualized in Fig. 2, the higher occupied molecular orbital is concentrated in the donor aminophenyl fragment of the molecule, while the lower unoccupied orbital is significantly distributed on the conjugated HTCP acceptor. This distribution demonstrates the possibility of efficient electron transfer from the donor part of the molecule to the acceptor upon excitation.

The electrochemical properties of the obtained compounds **3a–g** were studied by cyclic voltammetry (Fig. 4).

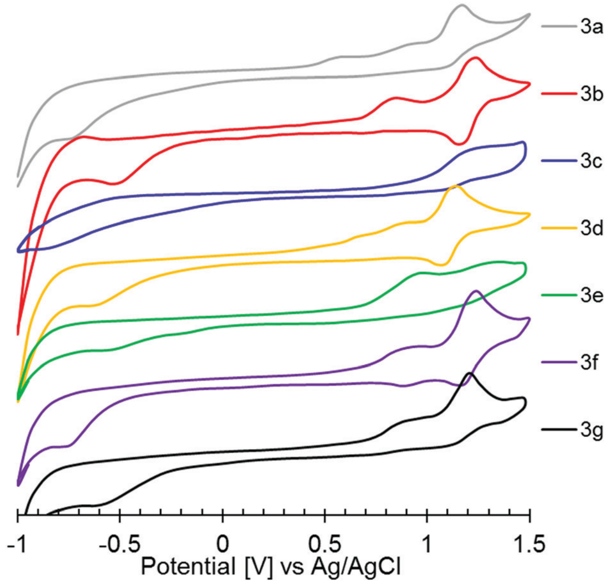


Fig. 4 Cyclic voltammograms of the synthesized compounds **3a–g** 1 mM, MeCN, 0.1 M TBAPF, 50 mV s^{-1}.

The energy of the higher occupied molecular orbital (HOMO) was calculated using the oxidation potential ($E_{\text{ox}}^{\text{onset}}$). Since the reduction process turned out to be quasi-reversible, the band gap (E_g) was refined using the electronic spectra of solutions of compounds **3a–g** in acetonitrile recorded on a spectrophotometer. The energy of the lowest unoccupied molecular orbital (LUMO) was found from the values of HOMO and E_g. The obtained results are summarized in Table 2.

The found and calculated values of the band gap of compounds **3a–g** are in the range of 2.37–2.42 and 2.86–2.95 eV, respectively. The found LUMO energies range from −2.46 to −2.97 eV and the calculated ones are of −2.89 to −2.97 eV, which are higher than the edge of the conduction band of titanium dioxide (−4.4 eV). The parameters indicate the possibility of efficient electron transfer from the HOMO of dyes **3a–g** to the conduction band of the semiconductor if the compounds are used as sensitizers. The smallest band gap was found for compounds **3a**, **3c**, and **3d**, with a diethylamine, piperidine, and pyrrolidine moiety in the para position of the phenyl substituent, respectively. The introduction of other electronegative heteroatoms in the substituent leads to an increase of the band gap. The oxidation potentials of compounds **3b**, **3c**, and **3e–g** are higher than the standard redox potential of the triiodide/iodide couple in acetonitrile, which demonstrates the possibility of dye regeneration by an electrolyte containing this redox couple.

Conclusion

Thus, a series of **4-amino-C$_6$H$_4$-HTCP** donor–acceptor chromophores, namely 2-(3-cyano-5-hydroxy-5-methyl-4-(4-aminophenyl)-1,5-dihydro-2*H*-pyrrol-2-ylidene)malononitriles **3a–g**, were synthesized by the interaction of 2-(3-cyano-4-(4-fluorophenyl)-5-hydroxy-5-methyl-1,5-dihydro-2*H*-pyrrol-2-ylidene)malononitrile with secondary amines at room temperature. For the obtained compounds the optical absorption was studied and the HOMO and LUMO energies and the band gap (E_g) were estimated using both theoretical calculations and experiments. The obtained data on the electrochemical and optical properties of compounds **3a–g** show the promise of the further study of these compounds as components of electro-optical materials.

Conflicts of interest

There are no conflicts to declare.

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