Proquinoid acceptors as building blocks for the design of efficient π-conjugated fluorophores with high electron affinity

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The association of aromatic electron donor groups with proquinoid acceptors leads to π-conjugated fluorophores combining tunable emission wavelength at constant geometry, high fluorescence efficiency and high electron affinity.
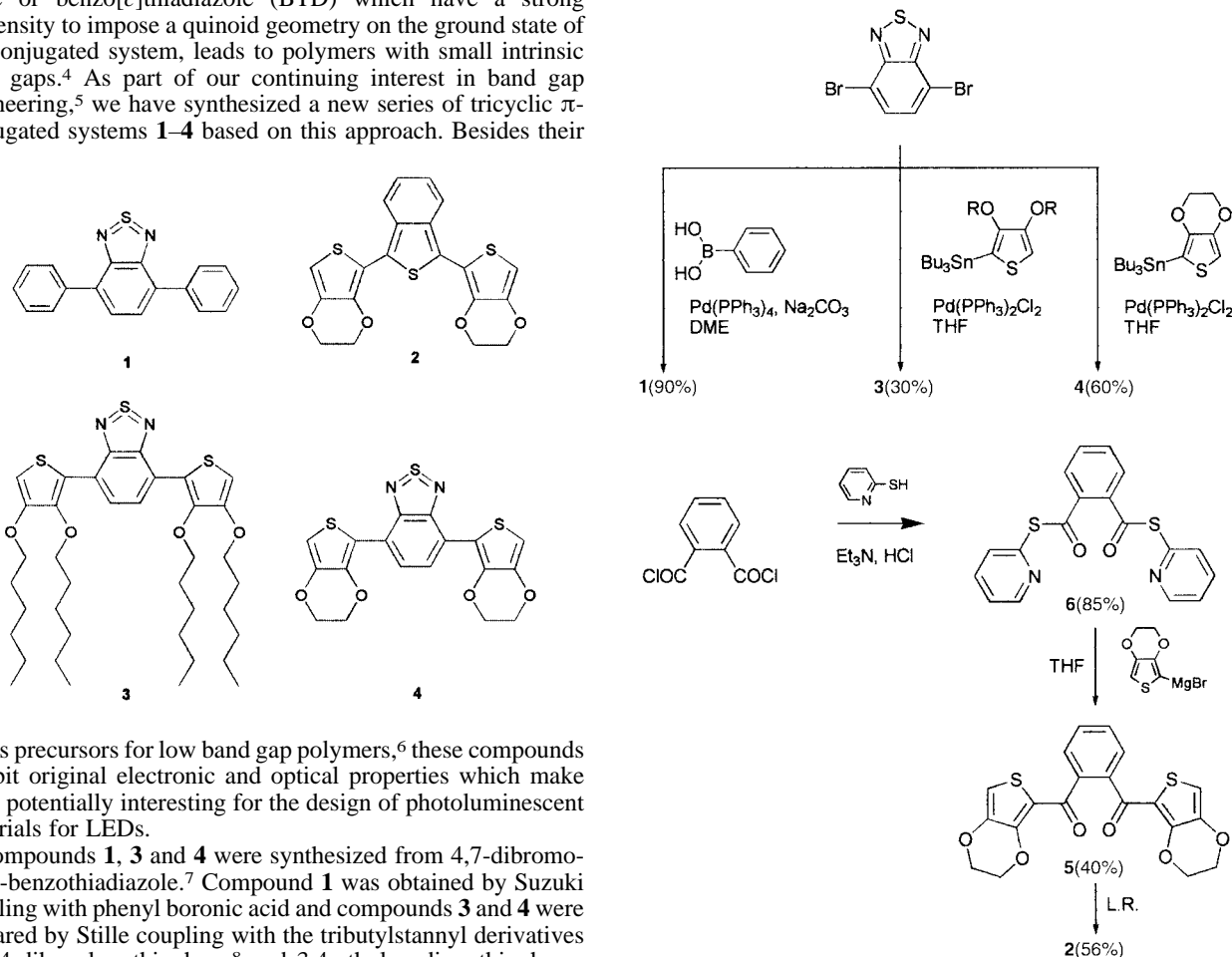
Conjugated fluorophores usable as active materials for light emitting diodes (LEDs) should ideally combine high emission quantum yields, tunable emission spectra and high electron affinity in order to allow electron injection from stable metal cathodes.[1]

The difficulty of meeting these various prerequisites with a single compound has given rise to specific synthetic approaches. Thus, control of the emission wavelength has been realized by adjusting the conjugation length of the fluorophore,[1,2] while increases in electron affinity have been achieved by incorporation of electron deficient groups, such as *e.g.* cyano or oxadiazole, in the π-conjugated system.[1,3]

It has been shown that the association of five-membered heterocycles with electron-deficient systems such as thienopyrazine or benzo[*c*]thiadiazole (BTD) which have a strong propensity to impose a quinoid geometry on the ground state of the conjugated system, leads to polymers with small intrinsic band gaps.[4] As part of our continuing interest in band gap engineering,[5] we have synthesized a new series of tricyclic π-conjugated systems **1–4** based on this approach. Besides their

use as precursors for low band gap polymers,[6] these compounds exhibit original electronic and optical properties which make them potentially interesting for the design of photoluminescent materials for LEDs.

Compounds **1**, **3** and **4** were synthesized from 4,7-dibromo-2,1,3-benzothiadiazole.[7] Compound **1** was obtained by Suzuki coupling with phenyl boronic acid and compounds **3** and **4** were prepared by Stille coupling with the tributylstannyl derivatives of 3,4-dihexyloxythiophene[8] and 3,4-ethylenedioxythiophene, respectively (Scheme 1). Compound **2** was prepared using a

procedure already described for the synthesis of 2,5-dithienyl-benzo[*c*]thiophene.[9] Reaction of phthaloyl chloride with 2-mercaptopyridine led to 1,2-bis[*S*-(2-pyridyl)]benzenedithioate **6** which was then reacted with 3,4-ethylenedioxy-2-thienylmagnesium bromide to give diketone **5**. Compound **2** was then obtained by ring closure with the Lawesson reagent (L.R.). Compounds **1–4** have been characterized by ^{1}H and ^{13}C NMR spectroscopy, mass spectrometry and elemental analysis.†

Table 1 lists the cyclic voltammetric (CV) and optical data for compounds **1–4**. Literature data for terphenyls (**3P**) and terthienyl (**3T**) have been included for comparison. Compounds **1–4** are reversibly reduced to their anion radicals and irreversibly oxidized owing to electropolymerisation. The values of the absorption maximum (λ_{max}) and HOMO–LUMO gap, ΔE (estimated from the absorption edge), for **3P** and **1** show that replacement of the median phenyl ring by the BTD group produces a 100 nm red shift of λ_{max} and a 1.10 eV decrease in ΔE. Comparison of the anodic peak potentials (E_{pa}) for **3P** and **1** shows that the BTD group scarcely affects the oxidation

Scheme 1

Table 1 CV[a] and optical[b] data for compounds **1**–**4**

Compd.	E_{pa}/V	E_{pr}/V	λ_{max}/nm	$\Delta E/eV$	λ_{em}/nm	ϕ_f
3P	1.80[c]	−2.70[c,d]	279[e]	3.97	339[e]	0.93[e]
1	1.82	−1.36	380	2.87	490	0.80
3T	1.10	−2.00[f]	350	3.05	430	0.066[g]
2	0.56	−1.80	450	2.33	613	0.92
3	1.06	−1.28	456	2.29	542	0.73
4	0.92	−1.40	481	2.19	630	0.75

[a] In 0.1 M NBu$_4$PF$_6$–MeCN, ref. SCE, 100 mV s^{-1}. [b] In CH$_2$Cl$_2$. [c] *vs.* Ag/AgCl (ref. 11). [d] In NBu$_4$Br–DMA (ref. 11). [e] In cyclohexane (ref. 12). [f] In NBu$_4$–DMF (ref. 13). [g] In dioxane (ref. 14).

potential but produces a positive shift of the reduction peak potential (E_{pr}) by more than 1.30 V, indicating a considerable increase in electron affinity.

As expected, thiophene-based compounds exhibit smaller ΔE values than **1** owing to the lower resonance energy of thiophene and the electron releasing effect of the alkoxy groups.[5]

Comparison of the optical data for **3T** and **2** shows that the combined effects of replacement of the median thiophene by benzo[*c*]thiophene and electron-releasing ethylenedioxy substituents produce a *ca.* 100 nm red shift of λ_{max} associated with a 0.70 eV decrease in ΔE. On the other hand, the 0.54 V decrease in E_{pa} and the 0.20 V positive shift of E_{pr}, indicated by the CV data, show that the gap reduction is essentially related to raising of the HOMO level.

Further replacement of the benzo[*c*]thiophene in **2** by the BTD group (**3** and **4**) produces a 6–31 nm red shift of λ_{max} and a small decrease in ΔE. However, the 0.40–0.50 V parallel positive shift of both E_{pa} and E_{pr} shows that the BTD group induces major changes in the HOMO and LUMO levels, with again a large enhancement of electron affinity. The small decrease in ΔE from **3** to **4** and the slight negative shift of E_{pa} reflects the stronger electron-donating effect of the ethylenedioxy bridge compared to dialkoxy chains.[8]

The fluorescence properties of compounds **1**–**4** have been analyzed in CH$_2$Cl$_2$ and the emission quantum yields (ϕ_f) have been determined against anthracene in 95% EtOH for **1**, and perylene in 95% EtOH for **2**–**4**. Introduction of BTD in the **3P** system produces a 150 nm red shift of the emission maximum (λ_{em}) and a 50 nm increase in the Stokes shift. Whereas the effect of BTD on ϕ_f is difficult to evaluate due to the different experimental conditions, the measured value of 0.80 for **1** shows that ϕ_f remains high.

Comparison of the data for **3T** and **2**–**4** reveals a large red shift of λ_{em} (up to 200 nm for **4**) and a 70–80 nm increase in the Stokes shift for **2** and **4**. Furthermore, the three compounds exhibit a considerable increase in ϕ_f which reaches a value as high as 0.92 for **2**. The significant increase in ϕ_f compared to the analog of **2** based on unsubstituted thiophene (ϕ_f = 0.67),[10] underlines the strong effect of the ethylenedioxy substituents on the fluorescence efficiency.

To summarize, we have shown that the insertion of proquinoid acceptor groups in short-chain π-conjugated oligo-

mers leads to fluorophores with a unique combination of enhanced electron affinity, high fluorescence efficiency and ready control of the emission wavelength at constant chain length. In addition to the intrinsic interest of these compounds as a new class of efficient fluorophores, the above synthetic strategy could open interesting perspectives for the design of active molecular or polymeric materials for LEDs.

Notes and references

† **1**: yellow powder, mp 127–129 °C. δ_H(CDCl$_3$): 7.97 (dd, 4H, ^3J 8.39, ^4J 1.17 Hz), 7.80 (s, 2H), 7.56 (t, 4H, ^3J 7.51 Hz), 7.47 (t, 2H, ^3J 7.42 Hz). δ_C(CDCl$_3$): 154.1, 137.4, 133.3, 129.3, 128.6, 128.4, 128.1. Anal: found (calc.): C, 74.99 (74.98); H, 4.35 (4.20); N, 9.51 (9.72); S, 11.10 (11.15)%.

2: brown solid, mp 146–148 °C. δ_H(CDCl$_3$): 7.96 (m, 2H), 7.13 (m, 2H), 6.42 (s, 2H), 4.32 (m, 4H), 4.27 (m, 4H). MS: *m/z* (%) 414 (M$^+$; 100), 317 (60). HRMS: calc. 414.0058, found 414.0054. Anal: found (calc.): C, 57.58 (56.95); H, 3.49 (3.40); O, 16.02 (15.44); S, 22.96 (23.21)%.

3: orange solid, mp 79–80 °C. δ_H(CDCl$_3$): 8.39 (s, 2H), 6.37 (s, 2H), 4.10 (t, 4H, ^3J 6.60 Hz), 4.02 (t, 4H, ^3J 6.60 Hz), 1.82 (m, 4H), 1.70 (m, 4H), 1.50 (m, 4H), 1.36 (m, 12H), 1.24 (m, 8H), 0.92 (m, 6H), 0.84 (m, 6H). δ_C(CDCl$_3$): 152.8, 150.3, 144.9, 127.6, 124.5, 120.6, 98.2, 72.9, 70.0, 31.5, 30.1, 29.1, 25.8, 25.6, 22.6, 22.5, 14.1, 14.0. MS: *m/z* (%) 700 (M$^+$; 100), 615 (20), 531 (20). HRMS: calc. 700.3402, found 700.3412.

4: brown solid, mp 314 °C. δ_H(CDCl$_3$): 8.4 (1s, 2H), 6.55 (s, 2H), 4.44 (t, 4H), 4.31 (t, 4H). δ_C(CDCl$_3$): 152.3, 141.6, 140.2, 126.6, 123.6, 113.7, 101.9, 64.9, 64.3. Anal: found (calc.): C, 51.77 (51.91); H, 3.04 (2.90); N, 6.62 (6.73); O, 15.28 (15.37); S, 23.29 (23.09)%.

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