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Direct coupling of carbenium ions with indoles and anilines for the synthesis of cationic π -conjugated dyes[†]

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A C–C bond forming reaction occurs spontaneously between tris-(2,6-dimethoxyphenyl)carbenium ions and indoles/anilines. The carbocation acts both as an electrophile and an oxidant. Effective cationic π -conjugated dyes are formed resulting in a strong hyper- and bathochromism.

Donor-acceptor organic dyes play major roles in many active fields of research, from nonlinear optics to organic photovoltaics and electronics.¹ These “push-pull” molecules possess electron withdrawing and donating fragments connected usually by a conjugated bridge. In the field of dyestuff, triarylcarbenium ions are classical electron-poor chromophores and finding a protocol to attach an electron-rich moiety to them in a single reaction was thus deemed interesting. Herein, in this context, we report the direct C–C bond forming reaction between tris-(2,6-dimethoxyphenyl) carbenium **1**² and electron-rich indoles **2** and anilines **3** (Scheme 1 and Fig. 1). The carbenium ion acts both as an electrophile and an oxidant. Interestingly, the coupling can be improved by the addition of triaryl methane chloride additives that replace **1** as an oxidant. Of importance, modulation of the

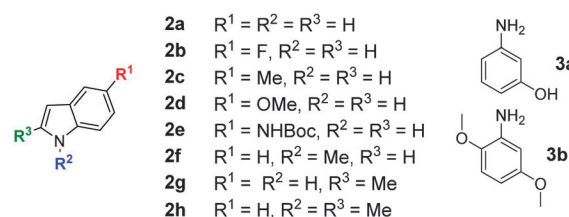
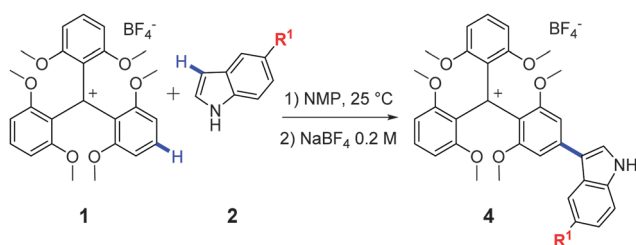


Fig. 1 Electron-rich indoles **2** and anilines **3**.

optical properties is achieved as strong hyper- and bathochromism results from the introduction of the electron-rich aromatic groups.

Tris-(2,6-dimethoxyphenyl)carbenium² **1** is an important member of the triaryl carbenium family of dyes.³ It is readily prepared in one step and on a large scale from dimethyl resorcinol.⁴ Compound **1** is the classic precursor to cationic [4]helicenes and triangulenes which are important chromophores and fluorophores with a broad spectrum of applications.⁵ For diverse purposes, it was necessary to prepare substituted analogues of **1**.^{4,5g,6} Prefunctionalized dimethyl resorcinols were then used and multistep syntheses were necessary in some instances.

As mentioned, a protocol for the direct functionalization of **1** was thus deemed interesting and, with the idea of forming donor-acceptor dyes, with electron-rich aromatic compounds such as



Scheme 1 Oxidative coupling between carbenium **1** and indoles **2**.

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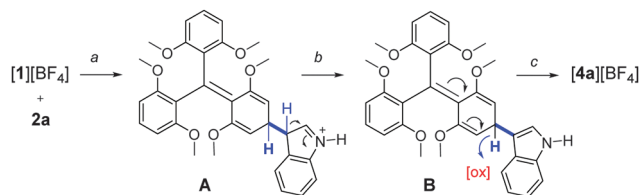
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Table 1 Oxidative coupling^a

Entry	Indole	Equiv. of 1	Time (h)	Additive	Product	Yield
1	2a	0.83	4	—	4a	47
2	2d	0.83	1	—	4d	42
3 ^b	2d	0.83	2	—	4d	45
4	2d	2.0	25	—	4d	77 ^c
5	2d	0.83	1	PMP ₃ CCl ^d	4d	74
6	2d	0.83	1	PMP ₂ PhCCl ^d	4d	79
7	2d	0.83	1	PMPPh ₂ CCl ^d	4d	76
8	2d	0.83	1	TrCl ^d	4d	64

^a Typical conditions: **1** (0.25 mmol), Indole (0.3 mmol), NMP (1 mL), 25 °C. ^b Under an argon atmosphere. ^c Yield based on indole molarity. ^d Additive: 0.28 mmol.



Scheme 2 (a) Nucleophilic attack at a *para*-position of **1**, (b) proton loss and rearomatization of the indole ring, (c) oxidative hydride removal and regeneration of the cationic core.

indoles and anilines in particular. In a first attempt, a solution of salt [1][BF₄] and indole **2a** was stirred in NMP at 25 °C (Table 1, entry 1). To our satisfaction, monitoring of the reaction revealed the rapid consumption of **1** in 4 hours and the desired salt [4a][BF₄] resulting from a C–C bond forming reaction was obtained in 47% yield. This result was confirmed using 5-OMe-indole **2d**. The corresponding indolyl-carbenium ion **4d** was obtained in one hour only with a similar yield of 42% (Table 1, entry 2).⁷ This formation of salts [4a][BF₄] and [4d][BF₄] was then best explained considering a vicarious (oxidative) nucleophilic substitution mechanism in three elemental steps (Scheme 2).⁸

First, a nucleophilic attack of electron-rich indoles **2a** or **2d** on the electrophilic cation **1** at the less hindered *para*-positions occurred to form intermediate **A** (step a). Then, rearomatization of the indole rings by proton loss leading to **B** occurred (step b). Finally, the removal of the *para*-C–H bond by oxidation to regenerate the cationic triaryl carbenium core (step c) was observed. Molecular oxygen was initially considered as the oxidant involved in step c but performing the reaction under an argon atmosphere did not change significantly the yield of the reaction (Table 1, entry 3). It was then considered that cation **1** was acting not only as an electrophile but also as an oxidant.⁹ This hypothesis was confirmed by ¹H-NMR spectroscopic analysis. In the crude reaction mixtures, the presence of neutral adduct **5** (Fig. 2) was detected along with products [4][BF₄].¹⁰ Compound **5** is clearly formed by hydride addition to the central carbon of **1**. With this result in hand, it is then easy to explain the better formation of [4d][BF₄] (77%, entry 4) with two equivalents of salt [1][BF₄]; one equivalent of **1** being consumed for the hydride removal, the other as an electrophile.¹¹

At that stage, to obtain better yields and avoid losing some of the starting cationic material, it was important to find a sacrificial oxidant that would be more reactive than **1** towards the hydride transfer and unreactive with indoles. A series of commercially available triaryl methane chloride derivatives was considered, namely tris-(4-methoxyphenyl)methyl chloride (PMP₃CCl), bis-(4-methoxyphenyl)phenylmethyl chloride (PMP₂PhCCl), (4-methoxyphenyl)-diphenylmethyl chloride (PMPPH₂CCl) and trityl (TrCl); all these compounds being *a priori* able to form under polar reaction conditions, the corresponding carbenium ions by dissociation of the C–Cl bond. To our satisfaction, all four reactions performed better with these additives (Table 1, entries 5 to 8). Yields were increased (64–79% vs. 42%) and the reaction times could be maintained to one hour only.¹² Out of the four compounds, PMP₂PhCCl was selected as the additive for further studies as cleaner crude reaction mixtures and slightly better yields were routinely obtained.

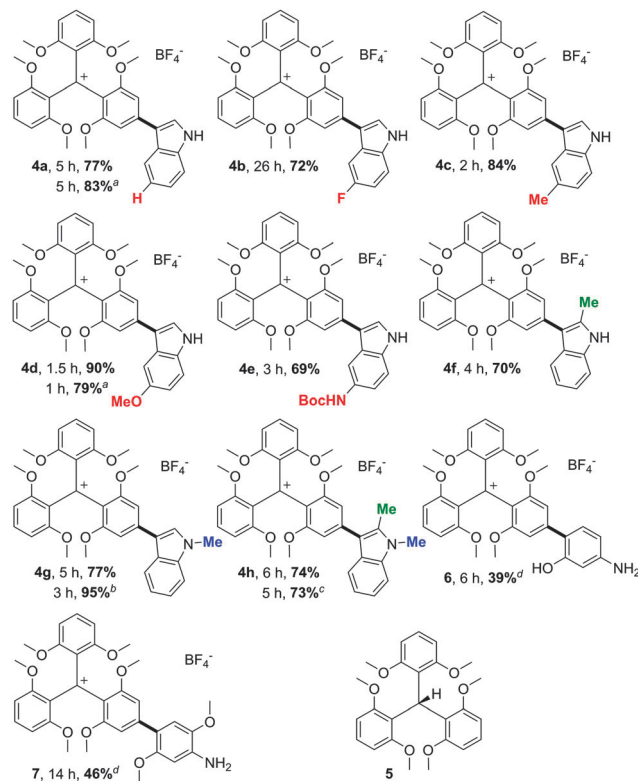


Fig. 2 Substrate scope and by-product **5**. Typical conditions: [1][BF₄] (0.5 mmol), PMP₂PhCCl (0.55 mmol), indole (0.55–0.83 mmol), NMP (1.5 mL), 25 °C. ^a 0.25 mmol scale of [1][BF₄]. ^b 1.5 mmol scale of [1][BF₄]. ^c 1.1 mmol scale of [1][BF₄]. ^d Without PMP₂PhCCl.

Various indoles (**2a** to **2h**) were then employed giving in all cases the respective indolyltriarylcarbenium tetrafluoroborate salts [4a][BF₄] to [4h][BF₄] in high purity and good yields (69–90%, Fig. 2).¹³ In the 5-substituted series, not too surprisingly, coupling was efficient with electron-rich indoles and more difficult with electron-deficient ones. In fact, a lack of coupling showed that 5-CN and 5-NO₂ indoles and a longer reaction time were required to obtain fluoro **4b** with full conversion. 1-Me and/or 2-Me indoles **2f**, **2g** and **2h** reacted on the other hand very well giving rise to corresponding cations **4f**, **4g** and **4h** in good yields (Fig. 2). The efficiency of the reaction seems in some cases to depend on the reaction scale for reasons that are not clear at the moment (*e.g.*, **4d** and **4g**). Finally, to verify the generality of the approach, the oxidative coupling was attempted with electron-rich 3-hydroxyaniline **3a** and 2,5-dimethoxyaniline **3b** to yield salts **6** and **7** (39% and 46% respectively). In these two examples, rather than the formation of the corresponding acridinium salts,¹⁴ C–C bond formation occurs exclusively *para* to the amino group on the nucleophile and *para* to the central carbon of **1**. Yields are however lower and the addition of PMP₂PhCCl did not improve the situation. With these compounds in hand, care was then taken to study and characterize the optical properties.

The electronic absorption spectra of the carbenium cation **1** and of all the substituted derivatives, **4**, **6** and **7**, are dominated by a broad absorption band located between 450 and 750 nm,

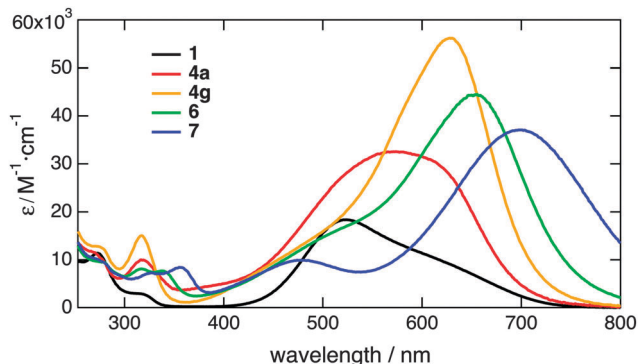


Fig. 3 Electronic absorption spectra of **1**, **4a**, **4g**, **6**, and **7** in acetonitrile.

with a shape and maximum that depend on the substituent (Fig. 3 and Table S1, ESI[†]).

To obtain more quantitative insight into the origin of this band, quantum chemistry calculations were performed on selected dyes. The ground-state geometry was first optimized at the density functional level of theory (DFT) and the electronic vertical excitation energies and oscillator strengths were then computed using time-dependent DFT (TD-DFT). For **1**, these calculations predict two pairs of transitions at 508–510 nm and at 428–429 nm with an oscillator strength of around 0.11–0.13. This quasi-degeneracy originates from the high symmetry of the optimized structure, and, thus, to several molecular orbitals (MOs), like *e.g.* the three highest occupied ones (HOMOs), with very similar energies ($\Delta E \leq 6$ meV). The first pair of transitions is predicted to arise from a mixing of one-electron excitations from all these three MOs to the lowest unoccupied MO (LUMO). Whereas each of the three HOMOs are localized on a different pair of dimethoxyphenyl branches (Fig. S3, ESI[†]), the LUMO is delocalized over the whole molecule. Despite the steric hindrance introduced by the methoxy substituents, rotation by $\pm 10^\circ$ of the dimethoxyphenyl groups around the single bond to the central carbon atom is possible at room temperature. Rotation of one of these groups leads to a lowering of the symmetry and a suppression of the quasi-degeneracy of the transitions. With such a $\pm 10^\circ$ distortion, the transitions are predicted to be at 520 nm and 500 nm. Therefore, apart from some possible overestimation of the transition energies, these calculations account well for the very broad absorption band of **1**.

The absorption band of **4a**, with the indole substituent, is more symmetric while remaining very broad, is shifted to lower energy by 50 nm (1600 cm^{-1}), and is more intense. TD-DFT calculations reproduce these differences, with predicted transitions at 595 nm and 556 nm, and an oscillator strength of 0.27 and 0.34, respectively. Both transitions originate from a mixing of HOMO \rightarrow LUMO and HOMO $- 2 \rightarrow$ LUMO excitations, the first, dominating the 595 transition, corresponding to a charge-transfer from the indole group to the triarylcarbenium centre, and the second, dominating the 556 nm transition, to a charge-transfer from the two other branches (Fig. 4). Substitution of the indole unit by methyl (**4c**, **4f**, **4g** and **4h**), methoxy (**4d**) or amino groups (**4e**) leads to a further red shift of the band.

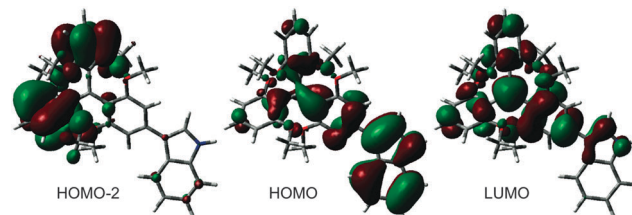


Fig. 4 Frontier molecular orbitals of **4a** calculated at the CAM-B3LYP/6-31G* level of theory.

This can be explained by the enhanced electron-donating properties of the indole and thus by the stabilization of the charge-transfer excited state relative to **4a**. Finally, replacing the indole by an aniline (**6** and **7**) also results in a red shift of the absorption band compared to **4a**. This shift can also be discussed in terms of a better electron donating ability of aniline compared to indole. This is further confirmed by the red shift observed upon going from **6** to **7**, *i.e.* by increasing the reducing properties of the aniline.

No stationary emission could be detected with any of the compounds in acetonitrile, pointing to a fluorescence quantum yield, Φ_f , smaller than $\sim 10^{-4}$. This is due to the extremely short excited-state lifetime of these molecules as revealed by femtosecond-resolved spectroscopic measurements with **4a** in acetonitrile that yields a value of 1 ps (Fig. 5 and ESI[†]). Such ultrafast excited-state dynamics is characteristic of triphenylmethane dyes, and is due to an efficient non-radiative deactivation to the ground state *via* the distortion of the molecule around the single bond to the central carbon atom.¹⁶ This process can be slowed down by increasing the viscosity of the environment, and in glycerol, a weak ($\Phi_f = 1.5 \times 10^{-3}$) but distinct stationary fluorescence with a maximum around 725 nm can be measured (Fig. 5).

In summary, a direct and efficient method to couple aniline-indoles with triaryl carbenium dyes has been developed under oxidative conditions. The resulting push-pull moieties present an interesting modulation of the absorption properties in favor of strong hyper- and bathochromisms. Further applications of

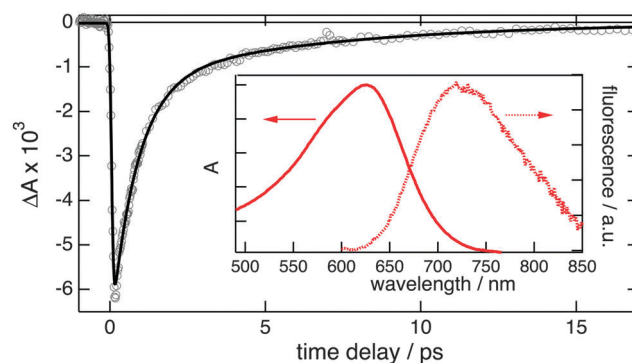


Fig. 5 Transient absorption profile at 555 nm measured with **4a** in acetonitrile after 400 nm excitation and reflecting the recovery of the ground-state population of the molecule. Inset: electronic absorption and fluorescence spectra of **4a** in glycerol.

this approach for the direct functionalization of dyes and fluorophores are being investigated.

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- See Fig. S1 in the ESI†.
- A longer reaction time was however required and purification of **4a** was cumbersome.
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