Synthesis, and the optical and electrochemical properties of a series of push–pull dyes based on the 4-(9-ethyl-9H-carbazol-3-yl)-4-phenylbuta-1,3-dienyl donor†

Corentin Pigot, Guillaume Noirbent, Thanh-Tuấn Bui, Sébastien Péralta, Sylvain Duval, Didier Gigmes, Malek Nechab and Frédéric Dumur

A series of twelve dyes based on the 4-(9-ethyl-9H-carbazol-3-yl)-4-phenylbuta-1,3-dienyl donor were prepared with electron acceptors varying in their structures but also in their electron-withdrawing ability. For specificity, a butadienyl spacer was introduced between the donor and the acceptor to both lower the bandgap and furnish dyes with high molar extinction coefficients. The different dyes A–N were characterized using various techniques including UV-visible absorption and fluorescence spectroscopy, and cyclic voltammetry. All dyes showed an intense intramolecular charge transfer band located in the visible range. To further investigate the optical properties of the twelve dyes, their solvatochromism was investigated in twenty-three solvents of different natures, enabling linear correlations to be obtained on different polarity scales such as the Taft, Reichardt and Catalan scales. To support the experimental results, the optical properties were compared with those theoretically determined.

A Introduction

During the past decades, organic dyes have attracted a great deal of interest from both the academic and industrial communities due to the numerous applications in which these structures can be used. Notably, organic dyes can be employed as singlet or triplet emitters for organic light-emitting diodes, as light-absorbing materials for organic photovoltaics (OPVs), as chromophores for non-linear optical applications, as dyes for various biological applications including cancer phototherapy or biological labelling, and as photoinitiators of polymerization, as singlet or triplet emitters for organic light-emitting structures can be used. Notably, organic dyes can be employed as singlet or triplet emitters for organic light-emitting diodes, as light-absorbing materials for organic photovoltaics (OPVs), as chromophores for non-linear optical applications, as dyes for various biological applications including cancer phototherapy or biological labelling, and as photoinitiators of polymerization, as singlet or triplet emitters for organic light-emitting structures can be used.

For many of the abovementioned applications, the possibility to design metal-free dyes is especially attractive, addressing the toxicity issue often raised by the use of transition metal complexes. For the design of organic molecules strongly absorbing in the visible range and displaying molar extinction coefficients on par with those of the transition metal complexes, push–pull dyes incorporating an electron donor connected to an electron acceptor by means of a π-conjugate spacer are the most obvious candidates and the most straightforward route to get molecules with high molar extinction coefficients. Indeed, the position of the intramolecular charge transfer (ICT) band can be easily tuned by modifying both the strength of the electron donating and the electron accepting abilities of the two groups attached at both ends of the π-conjugated spacer. This strategy is notably extremely useful to red-shift the ICT bands and thus reduce the HOMO–LUMO gap (where HOMO and LUMO respectively stands for highest occupied molecular orbital and lowest unoccupied molecular orbital). Additionally, the molar extinction coefficient can be drastically increased by elongating the π-conjugated spacer between the donor and the acceptor as a result of an improvement of the oscillator strength. However, elongation of the π-conjugation in these structures is not an easy task, as exemplified with the synthesis of 3-(9-alkyl-9H-carbazol-3-yl)acrylaldehydes. Indeed, for this aldehyde, only three syntheses are reported in the literature. In fact, carbazole is a remarkable electron donor exhibiting a relatively low oxidation potential, and good thermal stability and this polyaromatic structure can also be easily chemically modified. Carbazole is also a cheap compound.

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and so this structure was extensively used in Organic Electronics, with applications ranging from fluorescence emitters to host materials for OLEDs.55–58

While coming back to the synthesis of 3-(9-alkyl-9H-carbazol-3-yl)acrylaldehydes, the three procedures reported in the literature are based on metal-catalysed syntheses, namely the palladium-catalysed formylation of an alkenylzinc intermediate using S-(4-nitrophenyl)thioformate to introduce the aldehyde group for the synthesis of Cbz-1,59 the hydrozirconation homologation method of Maeta and Suzuki for the synthesis of Cbz-2,60 or the Pd-catalysed coupling reaction of acrolein diethyl acetal on a brominated carbazole for the synthesis of Cbz-3.61–63 (see Scheme 1). If large scale syntheses are required, these reactions are not adapted, requiring the use of multistep syntheses taking recourse to expensive catalysts, dry solvents and imposing a controlled atmosphere to proceed. Simpler synthetic methods are thus actively being researched. Recently, several studies were devoted to elaborate acrolein derivatives starting from benzophenone derivatives. This strategy was notably successfully applied to the synthesis of Michler’s aldehyde starting from Michler’s ketone.64,65 More recently, new benzophenone derivatives were also converted to their aldehyde analogues,66–71 furnishing dyes exhibiting a strong positive solvatochromism.72,73

In light of these results, a hybrid carbazole-based benzophenone Cbz-BP in which the electron donating ability is reinforced by the presence of the carbazole moiety has been converted to its aldehyde analogue Cbz-3. The approach used to access this extended electron donor by preparing first a carbazole–benzophenone adduct later converted as an acrylaldehyde is unprecedented. To the best of our knowledge, no such 3,3-diphenylacrylaldehyde derivative has been previously reported in the literature. However, the conversion of a carbazole–benzophenone adduct as an alkene has recently been reported in the literature.74 The different dyes were seen by a strong absorption extending over the visible range. These dyes were characterized using various techniques including UV-visible absorption and fluorescence spectroscopy and cyclic voltammetry. Theoretical calculations were also carried out to get a deeper insight into the electronic transitions involved in the optical transitions. Finally, solvatochromism of the 12 dyes was examined on several solvent polarities scales and linear correlations could be obtained using the Kamlet–Taft, Reichardt and Catalan empirical models.

![Scheme 1](image_url)  
**Scheme 1** Synthetic route to 3-(9-alkyl-9H-carbazol-3-yl)acrylaldehydes Cbz-1–Cbz-3.

![Fig. 1](image_url)  
**Fig. 1** Chemical structures of dyes A–N.
B Results and discussion

B1. Synthesis of the dyes

The extended aldehyde Cbz-BP has been synthesized in three steps starting from 9-ethyl-9H-carbazole. By performing a Friedel-Crafts reaction with benzoyl chloride in the presence of aluminum chloride, (9-ethyl-9H-carbazol-3-yl)(phenyl)methanone could be prepared in 84% yield. Addition of methylmagnesium iodide followed by a dehydration reaction furnished 9-ethyl-3-(1-phenylvinyl)-9H-carbazole in almost quantitative yield (see Scheme 2). Formylation of the alkenne by a Vilsmeier-Haack reaction gave Cbz-BP as a mixture of s-cis/s-trans isomers that could not be separated via column chromatography. All attempts of iodine-catalyzed thermal cis/trans isomerization in toluene did not allow the modification of the ratio between isomers.75 If no structural determination was carried out to identify which isomer was the main product, a 2:1 ratio could be found on the proton NMR spectrum of Cbz-BP. Interestingly, modification of the reaction time during the Vilsmeier-Haack reaction did not modify the ratio between isomers. Consequently, this mixture of isomers was subsequently used for the synthesis of the different dyes. Besides, in order to investigate the potential influence of the isomerization onto the optical properties, one of the two isomers could be obtained in almost pure form but in small quantity by crystallisation at −20 °C in a mixture of THF/pentane solvents.

Finally, eleven of the twelve dyes of the series were prepared via a Knoevenagel reaction carried out under basic conditions. Except for dyes B and E for which diisopropylamine (DIPA) was used instead of piperidine, all dyes could be obtained with reaction yields ranging from 78 to 92% (see Scheme 3). In the case of dyes B and E, the choice of DIPA as the base was motivated by recent results reported in the literature mentioning a nucleophilic attack of secondary amines on the cyano groups, inducing a cyclization reaction and producing azafluorenone derivatives.76–80 However, piperidine could be used for the synthesis of dye M, no nucleophilic attack of amine being reported at present in the literature for EA11. Finally, dye F was prepared by using a specific procedure. Indeed, due to the remarkable stability of the EA3 anion in basic conditions, no condensation reaction can occur. To circumvent this problem, the condensation of Cbz-BP and EA3 in acetic anhydride furnished dye F in 85% yield.

In the case of symmetric electron acceptors (EA1, EA3, EA4, EA6, EA7, EA8 and EA12), the corresponding dyes (A, C, F–J and N) were obtained as a mixture of s-cis and s-trans isomers. Conversely, a more complex situation was found for dyes prepared with EA2, EA5, EA9, EA10 and EA11, since in the complement of a s-cis/s-trans mixture, the different electron acceptors could adopt two different orientations so that a mixture of 4 isomers could be theoretically obtained in these cases (see Fig. 2). Besides, the steric hindrance induced by the use of asymmetric electron acceptors such as EA2 and EA5 certainly favour an orientation over the other. It has to be noticed that among the twelve electron acceptors issued in this study, EA2,81 EA3,82 EA4,83 EA5,76 EA1184 and EA1285 had to be prepared.

Interestingly, two isomers (D and I) could be isolated in pure form. Indeed, due to the marked insolubility of one of the isomers of dyes I, these could be easily separated from its mixture via precipitation. Conversely, in the case of dye D (which is a pure isomer of C), this latter was obtained by opposing the isolated isomer of Cbz-BP to EA1 under basic conditions. Finally, due to the exceptional electron-withdrawing ability of EA12, a spontaneous deprotonation can occur in highly polar solvents such as DMF. Therefore, N could be prepared at room temperature in DMF, without using a base, and obtained as a precipitate upon addition of pentane.

Scheme 3 Synthetic route to dyes A–N.

Scheme 2 Synthetic route to Cbz-BP.
to the reaction media. Dye N was isolated in the pure form by filtration, in 87% yield.

B2. Optical properties

All dyes showed good solubility in chloroform so that a comparison of their optical properties could be established. A summary of the optical properties is provided in Table 1 and Fig. 3 and 4. As shown in the Fig. 3, a severe variation of the absorption maxima with the electron-withdrawing ability of dyes A–N could be detected. Thus, absorption maxima ranging from 475 nm (K) to 587 nm (N) and 610 nm (B) were found. Position of the ICT bands underwent a redshift following the order of the electron acceptor strength. Notably, comparison of the absorption maxima between A and C revealed the elongation of the indane-1,3-dione-based acceptor EA4 to red-shift the absorption of A by ca. 30 nm compared to that determined for C comprising EA1 as the acceptor. Interestingly, a superimposition of the absorption spectra of A and J could be clearly evidenced, demonstrating that the electron-withdrawing abilities of 1H-cyclopenta[b]naphthalene-1,3(2H)-dione EA4 and 1,3-diethyl-2-thioxodihydropyrimidine-4,6(1H,5H)-dione EA8 were

Table 1 Optical characteristics of the different compounds in chloroform with the values theoretically determined in CH$_2$Cl$_2$. HOMO–LUMO gaps ($\Delta E$) are also shown in this table.

| Compounds | A     | B     | C     | D     | E     | F     | G     |
|-----------|-------|-------|-------|-------|-------|-------|-------|
| $\lambda_{\text{exp}}$ (nm) | 525   | 610   | 495   | 495   | 575   | 583   | 479   |
| $\lambda_{\text{theo}}$ (nm) | 495   | 559   | 475   | —     | 542   | 554   | 470   |
| $\varepsilon_{\text{exp}}$ (M$^{-1}$ cm$^{-1}$) | 42.600 | 57.750 | 36.400 | 35.900 | 40.300 | 37.700 | 35.400 |
| $\varepsilon_{\text{theo}}$ (M$^{-1}$ cm$^{-1}$) | 81.300 | 62.600 | 66.000 | —     | 63.300 | 93.000 | 46.700 |
| $\Delta E_{\text{exp}}$ (eV) | 2.36  | 2.03  | 2.50  | 2.50  | 2.15  | 2.12  | 2.59  |
| $\Delta E_{\text{theo}}$ (eV) | 2.51  | 2.22  | 2.61  | —     | 2.29  | 2.22  | 2.64  |

| Compounds | H     | I     | J     | K     | L     | M     | N     |
|-----------|-------|-------|-------|-------|-------|-------|-------|
| $\lambda_{\text{exp}}$ (nm) | 490   | 475   | 526   | 467   | 467   | 558   | 501, 587 |
| $\lambda_{\text{theo}}$ (nm) | 477   | —     | 506   | 487   | 487   | 550   | 517, 656 |
| $\varepsilon_{\text{exp}}$ (M$^{-1}$ cm$^{-1}$) | 45.100 | 43.200 | 61.600 | 49.600 | 47.300 | 55.100 | 51.300, 56.000 |
| $\varepsilon_{\text{theo}}$ (M$^{-1}$ cm$^{-1}$) | 54.400 | —     | 68.600 | 72.600 | 72.700 | 96.200 | 70.800, 89.000 |
| $\Delta E_{\text{exp}}$ (eV) | 2.53  | 2.61  | 2.36  | 2.65  | 2.65  | 2.22  | 2.11  |
| $\Delta E_{\text{theo}}$ (eV) | 2.60  | —     | 2.22  | 2.55  | 2.55  | 2.23  | 1.89  |

Fig. 2 The four possible isomers when asymmetric electron acceptors are used.

Fig. 3 Normalized UV-visible absorption spectra of dyes A–N in chloroform.
that a reduction of the conjugation between the two partners is

it can be confidently proposed that

than its analogue, on the basis of the UV-visible absorption spectra,

(see Fig. S1 and S2, ESI†) the calculations to give absorption

maxima to be in perfect agreement with the experimental one

coefficients (see Fig. S1, ESI†).

Interestingly, if the absorption spectrum of

isomer and the mixture could be established (see Fig. 5).

As anticipated, the highest molar extinction coefficients

could be found for the four dyes bearing the strongest electron

acceptors (EA5, EA8, EA11 and EA12), namely dyes B, J, M and

N. By increasing the electron acceptor strength, the oscillator

strength is logically increased, enhancing the molar extinction

coefficients (see Fig. S1, ESI†).

A comparison with the simulated UV-visible absorption spectra

in dichloromethane revealed the calculations to give absorption

maxima to be in perfect agreement with the experimental one

(see Fig. S1 and S2, ESI†). Finally, considering that 2 isomers

(D and I) could be separated from their respective mixtures (C and

H), a comparison between the absorption spectra of the isolated

isomer and the mixture could be established (see Fig. 5).

Interestingly, if the absorption spectrum of C perfectly super-

imposed that of D, a completely different behavior was found for

H and I, the ICT band of I being blue-shifted by 14 nm (476 nm vs.

490 nm for H). Considering that the isomer I is less conjugated than its analogue, on the basis of the UV-visible absorption spectra,

it can be confidently proposed that I is the s-cis isomer of H.

Additionally, in this configuration, the s-cis configuration

imposes an internal torsion inside the molecules due to the

steric hindrance generated by the donor and the acceptor so that a reduction of the conjugation between the two partners is

comparable, because the two dyes possessed the same
electron donor.

Among the different electron acceptors, the most interesting

one is undoubtedly EA12, which enables the design of a dye (N)

exhibiting two ICT bands located at 510 and 587 nm respectively.

For comparison, EA5 which is the strongest electron acceptor of

the series could only furnish a dye (B) with an absorption

maximum at 610 nm, and therefore only shifted by about

20 nm compared to dye N. Based on previous reports devoted

tetranitrofluorene-based dyes, the presence of the two intense

ICT bands detected in the UV-visible absorption spectrum of

N can be assigned to a significant intramolecular charge transfer

occurring in the ground state.86 In particular, due to the

presence of four electron withdrawing nitro groups onto TNF,

numerous mesomeric forms can be written, differing by the

length of the π-conjugated spacer between the nitro and the

amino groups (see Fig. 4).

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acceptors (EA5, EA8, EA11 and EA12), namely dyes B, J, M and

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it can be confidently proposed that I is the s-cis isomer of H.

Additionally, in this configuration, the s-cis configuration

imposes an internal torsion inside the molecules due to the

steric hindrance generated by the donor and the acceptor so that a reduction of the conjugation between the two partners is

logically observed. Considering that severe variations of the

absorption maxima were found by varying the electron-

withdrawing groups, the experimental behavior observed for
dyes A–N was rationalized by theoretical calculations.

B3. Theoretical calculations

The energy levels of the highest occupied molecular orbital

(HOMO) and the lowest unoccupied molecular orbital (LUMO)

were determined by theoretical calculations and a representative

set of the electronic distribution is provided in Fig. 6. As
evidenced in Fig. 6, a HOMO energy level specifically localized

on the carbazole group and a LUMO energy level comprising

both the acceptor and the lateral phenyl ring could be found for

all dyes. While examining the energy levels of both the HOMOs

and LUMOs of all dyes, almost no variation of the HOMO level

was found, consistent with a localization of the HOMO onto the
carbazole moiety (see Table 2). Conversely, major differences

could be found for the positions of the LUMO levels, resulting

from their localization onto the acceptor moieties. As a result of

this, the variation of the HOMO–LUMO gap only originates from

the variation of the positions of the LUMO levels. More precisely,

by improving the electron-accepting ability, the LUMO level is

stabilized, decreasing the HOMO–LUMO gap.

B4. Solvatochromism

Push–pull dyes are compounds that are highly sensitive to their

environment (polarity, and polarizability of the solvents) and

position of the ICT bands can drastically vary with the solvent

effects.87,88 Generally, for push–pull dyes, both HOMO and

LUMO energy levels are precisely localized onto two different

parts of the molecule. In the present case, a positive solvato-

chromism is typically observed, evidencing an important

charge redistribution upon photoexcitation and a dipole

moment larger in the excited state than in the ground state.

This behavior is typically found for push–pull dyes exhibiting a

relatively small dipole moment in the ground state, which is

achievable by separating the donor from the acceptor by an

elongated spacer.89–93 To investigate the solvatochromic

Fig. 5 Comparison of the UV-visible absorption spectra of C/D and H/I in

chloroform.

Fig. 4 Different mesomeric forms supporting the presence of two ICT

bands for the TNF-based dye N.
properties of dyes, numerous solvent polarity scales have been
developed over the years and the Kamlet–Taft’s,94 Dimroth–
Reichardt’s,95 Lippert–Mataga’s,96 Catalan’s,97,98 Kawski–
Chamma–Viallet’s,99 McRae’s,100 Suppan’s,101 and Bakhshiev’s102
scales can be cited as the most popular ones. Investigations of
the solvatochromic properties of dyes A–N were carried out in
23 solvents of different polarities and changes in the longest-
wavelength absorption maxima $\lambda_{\text{max}}$ for the 14 dyes are
summarized in Table 3. First, the intramolecular nature of
the charge transfer detected for all dyes was verified by realizing
successive dilutions and linear plots could be obtained by
measuring the absorbance vs. the dye concentration. This point
being verified, the resulting data were evaluated by means of
the different abovementioned empirical models. Interestingly,
remarkable correlations were obtained on the Kamlet–Taft
and the Catalan scales as well as, to a lesser extent, on the Reichardt
scale. In particular, for the Catalan, several parameters have
been developed such as the solvent polarizability (SP), the
solvent dipolarity (SdP) and the solvent polarity/polarizability
(SPP) parameters.103–105 In this work, the best correlations were
obtained with the Catalan SPP parameters taking into account
the polarity/polarizability of the solvents. This is also this
interaction, which is considered by the two other solvatochromic
scales, namely the Kamlet–Taft and the Reichardt models.
Therefore, the solvent–solute interactions are mainly governed
by the polarity/polarizability of the solvents, which was con-
firmed by three polarity scales based on these interactions.
Among all dyes, the best correlations were obtained for dyes B
or K, as shown in the Fig. 7.

![Fig. 6 Optimized geometries and HOMO/LUMO electronic distributions of dyes A, C and G.](image)

| Compounds | A | B | C/D | E | F | G |
|-----------|---|---|-----|---|---|---|
| HOMO (eV) | −5.55 | −5.48 | −5.56 | −5.71 | −5.83 | −5.69 |
| LUMO (eV) | −2.72 | −3.17 | −2.64 | −3.06 | −3.27 | −2.78 |

| Compounds | H/I | J | K | L | M | N |
|-----------|-----|---|---|---|---|---|
| HOMO (eV) | −5.64 | −5.71 | −5.66 | −5.67 | −5.95 | −5.90 |
| LUMO (eV) | −2.79 | −2.99 | −2.72 | −2.72 | −3.33 | −3.91 |
For all dyes, negative slope lines were found for the linear regressions, irrespective of the polarity scales, indicative of positive solvatochromism. Considering that the absolute value of the slopes can provide information of the sensitivity of the dyes to the solvent polarity and thus of the charge redistribution upon excitation, a summary of the different negative slope lines is provided in Fig. 8. Interestingly, in the series of 12 dyes, three different behaviors could be detected. Thus, only dyes E, F, H and N differ from the others for which similar slopes were found for both the Kamlet-Taft or the Catalan plots. Comparison between H and I is particularly interesting since I is a pure isomer isolated from H. Besides, a completely different behavior with regard to the solvent polarity was found, H exhibiting a lower sensitivity than I. These results confirm that I is certainly the s-cis isomer, and that the internal torsion induced by the steric hindrance between the donor and the acceptor are

Table 3  Summary of the optical properties of compounds A–H in solvents of various natures

| Compounds | A | B | C | D | E | F | G | H | I | J | K | L | M | N |
|-----------|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Acetone   | 510 | 585 | 456 | 456 | 533 | 546 | 456 | 466 | 462 | 460 | 456 | 457 | 534 | 562 |
| Acetonitrile | 508 | 579 | 489 | 476 | 550 | 545 | 461 | 466 | 463 | 504 | 455 | 456 | 526 | 561 |
| AcOE     | 502 | 581 | 479 | 477 | 552 | 551 | 457 | 465 | 458 | 499 | 455 | 455 | 525 | 561 |
| Anisole  | 516 | 591 | 491 | 489 | 562 | 573 | 471 | 474 | 466 | 508 | 464 | 464 | 549 | 582 |
| Butanol  | 525 | 604 | 498 | 497 | 569 | nd | 475 | 486 | 474 | 521 | 461 | 462 | 550 | 568 |
| Chloroform | 526 | 610 | 495 | 495 | 542 | 583 | 478 | 489 | 475 | 524 | 466 | 468 | 559 | 588 |
| Cyclohexane | 488 | 563 | 466 | 466 | 543 | 543 | 446 | 459 | 450 | 488 | 445 | 445 | 520 | 561 |
| 1,2-Dichloroethane | 515 | 592 | 488 | 488 | 564 | 576 | 468 | 479 | 470 | 516 | 462 | 465 | 551 | 586 |
| Dichloromethane | 517 | 597 | 489 | 489 | 548 | 577 | 471 | 480 | 469 | 514 | 463 | 464 | 553 | 586 |
| Diethyl carbonate | 499 | 575 | 474 | 475 | 547 | 546 | 456 | 462 | 459 | 496 | 452 | 452 | 521 | 553 |
| Diethyl ether | 496 | 572 | 472 | 469 | 548 | 547 | 451 | 462 | 455 | 497 | 453 | 451 | 528 | 568 |
| Diglyme | 508 | 588 | 483 | 483 | 559 | 574 | 463 | 471 | 466 | 511 | 461 | 461 | 545 | 569 |
| 1,4-Dioxane | 503 | 573 | 477 | 477 | 548 | 546 | 458 | 467 | 459 | 501 | 454 | 456 | 525 | 559 |
| Dimethylacetamide | 516 | 595 | 488 | 491 | 564 | 577 | 470 | 472 | 471 | 518 | 466 | 466 | 542 | 568 |
| Dimethylformamide | 517 | 596 | 489 | 488 | 560 | 576 | 469 | 472 | 468 | 512 | 463 | 465 | 539 | 577 |
| DMSO | 524 | 598 | 493 | 495 | 565 | 580 | 474 | 476 | 471 | 516 | 463 | 468 | 541 | 581 |
| Ethanol | 522 | 596 | 492 | 491 | 563 | nd | 475 | 480 | 466 | 517 | 458 | 459 | 548 | 574 |
| Heptane | 485 | 560 | 464 | 464 | 539 | 539 | 443 | 457 | 446 | 485 | 442 | 442 | 514 | nd |
| Nitrobenzene | 528 | 617 | 500 | 502 | 579 | 587 | 479 | 488 | 481 | 528 | 473 | 473 | 568 | 562 |
| THF | 507 | 583 | 482 | 478 | 556 | 563 | 460 | 467 | 460 | 503 | 458 | 458 | 533 | 567 |
| Toluene | 509 | 581 | 483 | 483 | 551 | 554 | 464 | 471 | 465 | 506 | 459 | 460 | 527 | 567 |
| Triethylamine | — | nd | 470 | 470 | nd | nd | 455 | 467 | 455 | nd | 450 | 450 | 522 | nd |
| p-Xylene | 508 | 572 | 479 | 479 | 553 | 550 | 462 | 468 | 456 | 504 | 458 | 459 | 528 | 569 |

\(^a\) Position of the ICT bands are given in nm. \(^b\) nd: not determined.

For all dyes, negative slope lines were found for the linear regressions, irrespective of the polarity scales, indicative of positive solvatochromism. Considering that the absolute value of the slopes can provide information of the sensitivity of the dyes to the solvent polarity and thus of the charge redistribution upon excitation, a summary of the different negative slope lines is provided in Fig. 8. Interestingly, in the series of 12 dyes, three different behaviors could be detected. Thus, only dyes E, F, H and N differ from the others for which similar slopes were found for both the Kamlet-Taft or the Catalan plots. Comparison between H and I is particularly interesting since I is a pure isomer isolated from H. Besides, a completely different behavior with regard to the solvent polarity was found, H exhibiting a lower sensitivity than I. These results confirm that I is certainly the s-cis isomer, and that the internal torsion induced by the steric hindrance between the donor and the acceptor are...
drastically modified by the polarity of the solvents. Conversely, C and its pure isomer D show similar slopes in both plots. Based on the NMR experiments, similarity of behaviors between C and D arises from the fact that D is mostly composed of C, resulting in a minor contribution of the other isomer on the optical properties. A lower sensitivity to the solvent polarity is also found for dyes E and N what is counter-intuitive considering that these two dyes possess strong electron acceptors. Finally, the most negative slopes were determined for dye F bearing EA3 as the acceptor. This pronounced sensitivity to the solvent polarity can be assigned to the presence of the numerous cyano groups on EA3, favoring a major redistribution of the electronic density upon excitation when highly polar solvents are used.

B5. Photoluminescence spectroscopy

The emission properties of all dyes were examined in chloroform as the solvent. Since almost all compounds were fluorescent, and were therefore not sensitive to oxygen, all experiments were carried out in air. Most of the dyes were photoluminescent so that a Stokes shift could be determined for most of the dyes. In addition, as shown in Fig. 9, by determining the crossing point between the UV-visible and the fluorescence spectra of each dye, energy of the first singlet excited state \( E_{S1} \) could be determined. All data are summarized in Table 4.

Carbazoles are known to be fluorescent compounds which explains why the different dyes were emissive. Only dye N comprising a TNF moiety as the acceptor was not emissive. The lack of photoluminescence of compound N can be attributed to the presence of the nitro groups, well-known to efficiently quench the photoluminescence of luminescent compounds. For all dyes, Stokes shift ranging from 50 nm for compound B to 97 nm for compound M could be determined. The largest Stokes shift was obtained for dye M comprising the 2-dicyanomethylidene-3-cyano-4,5,5-trimethyl-2,5-dihydrofuran (TCF) group as the acceptor. These large Stokes shifts are indicative of a significant electronic redistribution between the ground state and the excited state. Additionally, the fluorescence of the indane compounds (comprising EA1–EA5 as the electron acceptors) seems to be highly dependent of the number of the cyano functions. Indeed, the Stokes shift of F was only 61 nm while a Stokes shift of 68 nm and 78 nm could be respectively determined for compounds E and C/D. Indeed, due to the improved electron-withdrawing ability of EA2 compared to EA5, a reduction of the Stokes shift was detected, going from E (68 nm) to B (50 nm).

B6. Electrochemical properties

All push–pull dyes were investigated by cyclic voltammetry (CV) in deaerated acetonitrile solutions. The selected set of voltammograms is shown in Fig. 9 and all CV curves are given in the ESI. All the synthesized compounds exhibited irreversible single-electron oxidation and single-electron reduction processes. Concerning the oxidation, all the push–pull molecules were...
Table 5 Outline of the electrochemical properties of dyes A–N compared with DFT calculations. $E_{\text{onset}}$ correspond to all the oxidation potentials and $E_{\text{red}}$ the reduction potentials. $\Delta E_{\text{el}}$ corresponds to the difference between the HOMO and the LUMO levels, electrochemically obtained. Finally, $\Delta E_{\text{th}}$ is the difference between the HOMO and LUMO levels, theoretically obtained. Fc/Fc$^+$ was used as internal reference standard.

| Compounds | $E_{\text{onset}}$ (V per Fc) | $E_{\text{red onset}}$ (V per Fc) | $E_{\text{HOMO}}$ (eV) | $E_{\text{LUMO}}$ (eV) | $\Delta E_{\text{el}}$ (eV) | $\Delta E_{\text{th}}$ (eV) |
|-----------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| A         | 0.71            | −1.13           | −5.51           | −3.67           | 1.84            | 2.83            |
| B         | 0.76            | −1.00           | −5.56           | −3.80           | 1.76            | 2.31            |
| C         | 0.74            | −1.06           | −5.54           | −3.74           | 1.80            | 2.92            |
| D         | 0.74            | −1.14           | −5.54           | −3.66           | 1.88            | 2.92            |
| E         | 0.72            | −1.12           | −5.52           | −3.68           | 1.84            | 2.65            |
| F         | 0.74            | −0.95           | −5.54           | −3.85           | 1.69            | 2.56            |
| G         | 0.77            | −1.18           | −5.57           | −3.62           | 1.95            | 2.91            |
| H         | 0.75            | −1.14           | −5.55           | −3.67           | 1.93            | 2.85            |
| I         | 0.77            | −1.18           | −5.57           | −3.62           | 1.95            | 2.85            |
| J         | 0.75            | −1.07           | −5.55           | −3.73           | 1.82            | 2.72            |
| K         | 0.63            | −1.27           | −5.44           | −3.53           | 1.91            | 2.94            |
| L         | 0.63            | −1.29           | −5.44           | −3.51           | 1.93            | 2.95            |
| M         | 0.67            | −0.94           | −5.47           | −3.86           | 1.61            | 2.62            |
| N         | 0.69            | −1.18           | −5.49           | −3.62           | 1.87            | 1.99            |

*Onset of the oxidation and reduction potentials versus ferrocene ($E_{\text{onset}}$ vs. Fc). $E_{\text{HOMO}}$ and $E_{\text{LUMO}}$ were determined from the formulae: $E_{\text{HOMO}} = −4.8 - E_{\text{Fc}}$ vs. Fc and $E_{\text{LUMO}} = −4.8 - E_{\text{red}}$ vs. Fc.$^{113}$ $E_{\text{HOMO}}$ and $E_{\text{LUMO}}$ are given in eV.

Table 6 Fluorescence properties of the different compounds recorded in chloroform.

| Compounds | $\lambda_{\text{ex}}$ (nm) | $\lambda_{\text{em}}$ (nm) | $S_1$ (eV) | $E_{\text{ox onset}}$ (V vs. Fc) | $E_{\text{red onset}}$ (V vs. Fc) |
|-----------|-----------------|-----------------|-----------|-----------------|-----------------|
| A         | 526             | 490             | 2.30      | 1.55            | −0.75           |
| B         | 610             | 475             | 2.05      | 1.55            | −0.75           |
| C         | 495             | 526             | 1.95      | 1.55            | −0.75           |
| D         | 495             | 2.28            | 1.25      | 1.55            | −0.75           |
| E         | 575             | 2.28            | 1.25      | 1.55            | −0.75           |
| F         | 583             | 2.28            | 1.25      | 1.55            | −0.75           |
| G         | 479             | 2.28            | 1.25      | 1.55            | −0.75           |
| H         | 500             | 2.28            | 1.25      | 1.55            | −0.75           |
| I         | 128             | 2.28            | 1.25      | 1.55            | −0.75           |
| J         | 205             | 2.28            | 1.25      | 1.55            | −0.75           |
| K         | 129             | 2.28            | 1.25      | 1.55            | −0.75           |
| L         | 870             | 2.28            | 1.25      | 1.55            | −0.75           |
| M         | 147             | 2.28            | 1.25      | 1.55            | −0.75           |
| N         | 163             | 2.28            | 1.25      | 1.55            | −0.75           |
| O         | 198             | 2.28            | 1.25      | 1.55            | −0.75           |
| P         | 120             | 2.28            | 1.25      | 1.55            | −0.75           |

The largest reduction potential was observed for P, presumably resulting from the redox of the nitro groups prior to the central double bond. Reduction of the nitro groups is frequently observed in the case of poly(nitrofluorene) structures, explaining the difference of 200–500 mV observed between the reduction peak of this compound and that of the other dyes.$^{114,115}$

Finally, by using the ferrocene (Fc) ionization potential value as a standard and the equation established by Pommerehne et al., energy levels of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) could be estimated from the redox potentials (see Table 5).$^{116}$

Fig. 10 Cyclic voltammograms of I (up) and M (down) in acetonitrile solutions (10$^{-3}$ M) using tetrabutylammonium perchlorate (0.1 M) as the supporting electrolyte. Scan rate: 100 mV s$^{-1}$.

Fig. 11 Comparison between frontier orbital energy levels obtained from cyclic voltammetry and DFT calculations.
Thanks to the determination of the HOMO and LUMO energy levels by electrochemistry, a comparison could be made between the experimental and the theoretical values of the two energy levels (see Fig. 11). If a clear difference can be noticed between the LUMO\textsubscript{DFT} and the LUMO\textsubscript{el}, conversely, a good adequation between the theoretical and the experimental energy level of the HOMO orbital was found, as shown in the Fig. 11. Even if the position of the LUMO energy levels was overestimated by theoretical calculations, similar variations were found between the LUMO\textsubscript{DFT} and the LUMO\textsubscript{el}. This difference can be attributed to the fact that influence of the solvent on the LUMO energy level is not fully considered in the calculations.

C Conclusions
To conclude, a series of 12 push–pull dyes differing by the electron-acceptors have been designed and synthesized. Interestingly, the carbazole-based electron donor reported in this work has been synthesized for the first time according to a multistep synthesis. All dyes prepared using this electron donor proved to be soluble in most of the common organic solvents, even if electron acceptors such as (thio)barbituric acids and tetrani trofluorene derivatives well known to produce low soluble dyes have been used. By modifying the electron acceptors, a set of dyes absorbing over the whole visible range have been obtained. For all dyes, a positive solvatochromism could be determined, evidencing that the excited state of the dye is more polar than the ground state. If promising results have been obtained with this electron donor, the asymmetry of this electron-acceptors have been designed and synthesized.

Conflicts of interest
There are no conflicts to declare.

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