Dyes with tunable absorption properties from the visible to the near infrared range : 2,4,5,7-tetranitrofluorene (TNF) as a unique electron acceptor

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Abstract:

Fourteen dyes based on 2,4,5,7-tetranitrofluorene (TNF) as the electron acceptor have been designed and prepared in a one-step synthesis. By modifying the electron donor, optical properties of the dyes could be efficiently tuned and an absorption ranging between 450 nm and 700 nm could be determined by UV-visible absorption spectroscopy. To get a deeper insight into the optical properties, solvatochromism of the fourteen dyes has also been examined. For all dyes, a positive solvatochromism was determined using different solvent polarity scales such as the Kamlet-Taft and the Catalan empirical scales. Finally, electrochemical properties were also examined, and a comparison of the electrochemical and optical bandgaps could be established. Theoretical calculations were also performed to characterize the different dyes.

Keywords : Push-pull dyes; chromophore; tetranitrofluorene; TNF; solvatochromism; Knoevenagel reaction; near infrared absorption; mechanosynthesis

1. Introduction

In recent years, push-pull dyes have been the focus of intense research efforts due to the wide range of applications requiring these dyes. Among applications, Non-Linear Optics (NLO),[1-2] Organic Fields Effects Transistors (OFETs),[3] Organic Solar Cells (OPVs)[4-5] , photopolymerization[6-22], biological labeling,[23-26] mechanochromism,[27-30] fluorochromism,[31-34] or Organic Light-Emitting Diodes (OLEDs) [35] can be cited as the most common applications for organic dyes. Push-pull dyes are typically composed of an electron donor connected to an electron acceptor by mean of a π -conjugated and planar spacer.[36-37] Benefiting from the reciprocal interaction of the donor and the acceptor by mean of the conjugated spacer, compounds with fascinating properties can be obtained. Notably, malononitrile **1**,[38] substituted tricyanopropenes **2**,[39] 1,1,3-tricyano-2-substituted propenes **3**,[40] dicyanovinyl-thiophen-5-ylidenes **4**,[41] 2-(3-cyano-4,5,5-trimethylfuran-2(5H)-ylidene)malononitrile (TCF) **5**,[42] pyran derivatives **6** and **7**,[43,44] dicyanoimidazoles **8**,[45] pyrazines **9**,[46] hydantions and rhodanines **10**,[47] (thio)barbituric derivatives **11**,[48] isoxazolones **12**,[49] Meldrum derivatives **13**,[50] indanedione derivatives **14**,[51] **15**,[52,53] benzo[*d*]thiazoliums **16**,[54] benzo[*d*]imidazoliums **17** [55] and pyridinium **18**[56] can be cited as the common electron acceptors. However, design of push-pull dyes is not limited to the

design of chromophores starting from benchmark electron donors and acceptors, and a great deal of efforts is currently devoted to develop original donors and acceptors.[57]

Figure 1. Chemical structures of the most common electron acceptors 1-18.

Among all electron acceptors reported in the literature, 2,4,5,7-9*H*-tetranitrofluorene (TNF) is really a unique candidate for the design of push-pull dyes. As specificity, this electron acceptor is not commercially available, supporting the fact that a limited number of reports has been devoted to examine the optical properties of the TNF-based dyes. Besides, this electron acceptor is of interest. Indeed, as shown in the Figure 2, this electron acceptor which possesses a strongly acidic methylene group is capable to spontaneously deprotonate in highly polar solvents such as *N,N*-dimethylformamide (DMF), furnishing an anion exhibiting a significant absorption band in the near infrared (NIR) region.[58] Therefore, from this viewpoint, TNF is a promising candidate for the design of near-infrared dyes, when opposed to the appropriate electron donor.

Figure 2. UV-visible absorption spectra of 2,4,5,7-9*H*-tetranitrofluorene (left) and 2,4,7-trinitro-9*H*-fluorene (right) in *N,N*-dimethylformamide (DMF). Reproduced with permission from Noirbent et al. [58]. Copyright 2018 MDPI

By the presence of its activated methylene group, push-pull dyes based on TNF can also be prepared with one of the simplest reactions of Organic Chemistry, namely the Knoevenagel reaction.[59-63] Beyond the simple control of the absorption wavelengths, the synthetic procedure used to access to the targeted molecules is increasingly to be considered. In this field, mechanochemistry offers a unique opportunity to synthesize molecules under inexpensive, safe and environmentally friendly conditions, without making use of solvents and with shorter reaction times than those required for the same reaction done in solution.[64,65] The mechanical energy brought to promote the chemical changes is also a traceless reagent so that mechanochemistry is a powerful tool for Green Chemistry. From a synthetic point of view, the Knoevenagel reaction can be considered as a model reaction, simply involving two reactants and a catalyst, and finally releasing after reaction a water molecule.[66] In this article, 2,4,5,7-*H*-tetranitrofluorene (TNF) was used to design 14 push-pull dyes (See Figure 3).

Figure 3. Chemical structures of **PP1-PP14** made with TNF as the electron acceptor and examined in this study.

Photophysical properties of the 14 dyes as well as their electrochemical properties have been studied in detail. To support the experimental results, theoretical calculations were made. Finally, the solvatochromic properties were also examined. Preliminary experiments in mechanochemistry will also be presented using two different methodologies, the manual version by grinding the reagents in an agate stone mortar with a pestle or an automatized version making use of a ball Mixer Mill.

2. Results and Discussion

2.1. Synthesis of the dyes PP1-PP14

All dyes **PP1-PP14** presented in this work have been synthesized by a Knoevenagel reaction involving the aldehydes **D1-D14** and TNF as the electron acceptor (See Scheme 1). Knoevenagel reactions are most of the time performed in ethanol using piperidine as the catalyst. It has to be noticed that this procedure has been reported as soon as 1896 by Knoevenagel to condense benzaldehyde onto ethyl acetoacetate.[67] However, the Knoevenagel reaction is also reserved to electron acceptors possessing an activated methylene group and recently, several reports have highlighted the drawbacks related to the use of piperidine as the base. Thus, for cyano-based electron acceptors, an unexpected nucleophilic addition of piperidine onto the electron acceptors has been clearly evidenced in several reports.[68-72] Therefore, the development of procedure avoiding the use of base are actively researched. Interestingly, in the case of this strong electron acceptor (TNF), all reactions could be performed in catalyst-free conditions, using *N,N*-dimethylformamide (DMF) as the solvent, as previously reported by Perepichka and coworkers [73,74] (See Scheme 1).

Scheme 1. Synthetic pathways to **PP1-PP14** and the fourteen aldehydes used in this study.

More precisely, due to the strong electron-accepting ability of TNF, this electron acceptor can spontaneously deprotonate in DMF so that no base is necessary. Therefore, by using this highly polar solvent, DMF could avoid the use of any additional base. **PP1-PP14** were obtained, after only a few minutes (for instance for **PP2** or **PP3**) or two hours of reaction (for instance for **PP4** or **PP5**) with reaction yields ranging from 73% yield for **PP13** to 95% for **PP12** (See Table 1). All compounds were obtained as solids after removal of DMF. By crystallization in an ether:pentane mixture, the work-up could be reduced to a simple filtration and washing with pentane could provide the targeted compounds in pure form. For all compounds, their chemical structures were investigated by ^1H , ^{13}C NMR, and HRMS spectroscopies (see Supporting Information).

Table 1. Reaction yields obtained for the synthesis of **PP1-PP14** in DMF solutions

Compounds	PP1	PP2	PP3	PP4	PP5	PP6	PP7
Reaction yields (%)	85	82	78	85	80	81	89
Compounds	PP8	PP9	PP10	PP11	PP12	PP13	PP14
Reaction yields (%)	92	79	83	84	95	73	86

In order to reduce the reaction time and the production of waste related to the use of large quantities of solvents which is sometimes difficult to remove, preliminary works were also carried out concerning the use of mechanosynthesis to produce these chromophores without solvent, by grinding the reagents with a pestle in an agate stone mortar or by using a ball mill grinding equipment, namely a Retsch MM400 Mixer Mill (vibrational frequency : 30 Hz, grinding time : 5 min., grinding jar size : 5 mL, 10 grinding balls with 5 mm diameter). For the synthesis of **PP1-PP8**, the reaction still requires the use of a catalyst to proceed, here, a few drops of DMF were necessary to produce the Knoevenagel reaction. To make an effective comparison between mechanosynthesis and the solution-phase synthesis, the reaction yields obtained in solution were compared to the conversion rates obtained during the various mechanochemical tests done for seven chromophores. The conversion rates were determined by exploiting the ^1H NMR spectrum of the mechanosynthesized compounds. By comparing the integration of the proton peak corresponding to the aldehyde of the electron donor with that of the alkene obtained in the “push-pull” compound located in a different part of the NMR spectrum, their respective integrations could be determined (see in Supporting Information). Indeed, for mechanochemistry, the solids obtained during the experiments were directly analyzed without any further treatment. These preliminary results are reported in the Table 2. Comparison of the conversion rates obtained using the manual and the ball mill grinding equipment revealed the formation of the different compounds with higher conversion rates by using of ball mill grinding, attributable to a better homogenization of the reagents in the grinding jar, compared to that obtained in a mortar. Parallel to this, the reproducibility of the reaction was lower by manual grinding as the mixture of the two reagents is more disorganized than in a grinding jar and the reaction rate is also strongly dependent of the manipulator. Besides, for the two methods, the conversion rates obtained for **PP1-PP8** were almost quantitative, ranging between 99% for **PP1** and **PP8** and 87% for **PP3** by ball-milling, and between 99% for **PP4** and **PP8** and 77% for **PP3**, for hand grinding. It has to be noticed that in the aforementioned examples, the aldehyde was a liquid so that it could be used as a solvent for TNF. In the case of **D7**, a severe reduction of the reaction yield was evidenced, this aldehyde being a solid. To illustrate this, the reaction yield was reduced to 9% when **PP7** was synthesized in an agate mortar. This yield could be increased up to 65% by using the ball mill grinding equipment. **D6**, **D9-D14** being solids, mechanochemistry proved to be ineffective to produce the different targeted dyes when only a few

drops of DMF were added. In these conditions, **D6**, **D9-D14** could not be prepared by mechanochemistry.

Table 2. Conversion rates obtained for the synthesis of **PP1-PP5** and **PP7-PP8**.

Method	Compounds	PP1	PP2	PP3	PP4	PP5	PP6	PP7	PP8
Mixer Mill MM400 ^a	Conversion rate (%)	99	98	87	98	99	99	65	99
Agate stone mortar ^b	Conversion rate (%)	92	90	77	99	96	93	9	99

^a mill Frequency: 30 Hz; reaction time: 5 minutes. ^b reaction time: 10 minutes

By comparing the reaction yields obtained by mechanochemistry and in solution phase chemistry, mechanosynthesis constitutes a unique tool to elaborate push-pull dyes in high yields. Especially, chromophores comprising 2,4,5,7-tetranitrofluorene as the electron acceptor can be synthesized under inexpensive, safe and environmentally friendly conditions, without any use of solvent and with short reaction times.

2.2. Optical Properties

The fourteen chromophores examined in this work are “push-pull” chromophores and such dyes are typically characterized by an intense absorption band detected in the visible or the near infrared range corresponding to the intramolecular charge transfer (ICT) band. All the compounds were analyzed by UV-visible spectroscopy in order to determine their absorption properties in chloroform. The different spectra are shown in Figure 4 and a summary of the absorption characteristics of the different dyes are provided in the Table 3. Surprisingly, UV-visible absorption spectra of **PP1-PP14** were characterized by two intense absorption bands detected in the visible range. This behavior is unusual, considering that only one ICT band is usually detected on the UV-visible absorption spectrum.[75] Noticeably, intensity of the two peaks differs from a dye to another one and these two bands can be attributed to intramolecular charge transfer bands (ICTs). As anticipated, improvement of the electron-donating ability of the donor red-shifted the two ICT bands so that an optimal situation was found for **PP10** bearing the strongest electron donor of the series, namely Michler’s aldehyde. Following **PP10**, **PP8** and **PP9** also showed absorption maxima at 627 and 644 nm, blue-shifted by ca 70 and 53 nm compared to that of **PP10** (697 nm).

Figure 4. UV-visible absorption spectra of **PP1-PP14** recorded in chloroform.

Table 3. Positions of the ICT bands for **PP1-PP14** in chloroform.

Compounds	PP1	PP2	PP3	PP4	PP5	PP6	PP7
$\lambda_{\max}(\text{nm})$	436, 497	431, 498	422, 489	411, 472	359, 454	412, 448	502, 596
$\Delta\lambda_1-\lambda_2$ (nm)	61	67	67	61	95	36	94
Compounds	PP8	PP9	PP10	PP11	PP12	PP13	PP14
$\lambda_{\max}(\text{nm})$	521, 627	544, 644	560, 697	457, 543	470, 541	498, 588	499, 580
$\Delta\lambda_1-\lambda_2$ (nm)	106	100	137	86	71	90	81

Positions of the two peaks is highly dependent on the strength of the electron donor used to prepare the dye. Thus, when weak electron donors are used, a smaller energy difference can be found between the two peaks, as exemplified with **PP1-PP7** ($\Delta\lambda_1-\lambda_2 \sim 60\text{-}70$ nm). Conversely, when strong electron donors are used in **PP8** and **PP9**, an energy difference ranging between 100 nm for **PP9** to 137 nm for **PP10** could be determined, clearly evidencing the crucial role of the distance between the nitro groups and the donor strength in the electronic delocalization.

Theoretical studies were also realized in order to investigate the energy levels as well as the molecular orbitals (M.O.) compositions of the different dyes. DFT calculations were performed for all dyes at the B3LYP/6-311G(d,p) level of the theory using Gaussian 09 programs to determine the transitions involved in the different absorption peaks. Dichloromethane was used as the solvent model with a polarizable continuum model (PCM).[76-82] Energies of the highest occupied molecular orbitals (HOMO) and the lowest unoccupied molecular orbital (LUMO) and as well as the main transitions involved in the different peaks are summarized in the Table 4. The simulated absorption spectra for **PP1-PP14** are shown in the Figure 5. Assignments of the electronic transitions and contributions in the different transitions reported in the Table 4 have been determined with the GaussSum 3.0 software.

As evidenced in the Table 4, numerous transitions can be theoretically detected in the visible range. While comparing the theoretical values and the experimental values of ICT1 and ICT2, the two peaks detected in the visible range for **PP1-PP14** mainly arise from HOMO-1 $\rightarrow$ LUMO, HOMO $\rightarrow$ LUMO+1 and HOMO $\rightarrow$ LUMO+2 transitions. In the case of strong electron donors, additional contributions of HOMO $\rightarrow$ LUMO+3 or HOMO $\rightarrow$ LUMO+4 can even be detected, as exemplified for **PP8-PP10** (See Table 4). Interestingly, similar absorption spectra were predicted for **PP1**, **PP4** and **PP6**, the three dyes possessing an electron-donating group in *para*-position of the electron donor (See Figure 5b). By improving the electron-donating ability in **PP2** or **PP3**, a red-shift of the ICT bands could be anticipated by theoretical calculations, perfectly fitting the experimental trend (See Figure 5c). Examination of the contour plots of the HOMO and LUMO orbitals of the different dyes revealed the HOMO energy levels to be located onto the electron-donating parts of the different dyes whereas the LUMO level was centered on the TNF acceptor (See Figure 6). Only a small overlap between the HOMO and LUMO orbitals could be detected for **PP1-PP14**. It has to be noticed that for all dyes except for **PP1** and **PP5**, contribution of the HOMO $\rightarrow$ LUMO+1 transition is higher than 95% for the ICT band detected at short wavelengths. For **PP1** and **PP5**, contribution of this transition is reduced to only 75 and 31% respectively. As shown by the contour plots of the LUMO and LUMO+1 orbitals of **PP1-PP12**, a remarkable similarity of the electronic distribution can be found between the two orbitals, favorable to an electronic transition towards LUMO+1.

Figure 5. Theoretical UV-visible absorption spectra of **PP1-PP14** in dichloromethane.

Table 4. Summary of the simulated absorption characteristics in dilute dichloromethane of the different compounds. Data were obtained in dichloromethane solutions.

Compounds	E_{HOMO} (eV)	E_{LUMO} (eV)	λ_{max} (nm)	Transitions
PP1	-6.705	-4.068	627	HOMO->LUMO (99%)
			481	HOMO-1->LUMO (23%)
				HOMO->L+1 (75%)

PP2	-6.510	-3.909	472	HOMO-1->LUMO (76%)
				HOMO->L+1 (23%)
			440	HOMO->L+2 (94%)
			687	HOMO->LUMO (99%)
			511	HOMO->L+1 (98%)
PP3	-6.586	-3.945	474	HOMO->L+2 (96%)
			446	HOMO-1->LUMO (95%)
			438	HOMO->L+3 (97%)
			693	HOMO->LUMO (99%)
			517	HOMO->L+1 (98%)
PP4	-6.781	-4.048	577	HOMO->L+2 (96%)
			451	HOMO-1->LUMO (97%)
			445	HOMO->L+3 (97%)
			422	HOMO->L+4 (94%)
			631	HOMO->LUMO (99%)
PP5	-6.928	-4.057	479	HOMO->L+1 (98%)
			445	HOMO->L+2 (95%)
			599	HOMO->LUMO (99%)
			470	HOMO-1->LUMO (67%)
				HOMO->L+1 (31%)
PP6	-6.855	-4.091	455	HOMO-1->LUMO (32%)
				HOMO->L+1 (67%)
			628	HOMO->LUMO (99%)
			478	HOMO->L+1 (98%)
			444	HOMO->L+2 (95%)
PP7	-6.985	-4.548	414	HOMO->L+3 (95%)
			403	HOMO->L+4 (95%)
			818	HOMO->LUMO (99%)
			583	HOMO-> L+1 (97%)
			538	HOMO-> L+2 (96%)
PP8	-6.035	-3.761	491	HOMO-> L+3 (98%)
			464	HOMO-> L+4 (95%)
			895	HOMO->LUMO (99%)
			619	HOMO->L+1 (95%)
			565	HOMO->L+2 (97%)
PP9	-6.034	-3.878	513	HOMO->L+4 (89%)
				HOMO->L+3 (8%)
			508	HOMO->L+3 (82%)
				HOMO-1->LUMO (6%)
				HOMO->L+4 (9%)
PP10	-5.735	-3.673	895	HOMO->LUMO (100%)
			619	HOMO->L+1 (95%)
				HOMO->L+3 (3%)
			566	HOMO->L+2 (97%)
			513	HOMO->L+4 (89%)
				HOMO->L+3 (8%)
			508	HOMO->L+3 (82%)
				HOMO-1->LUMO (6%)
				HOMO->L+1 (2%)
				HOMO->L+4 (9%)
			948	HOMO->LUMO (98%)

			779	HOMO-1->LUMO (99%)
			649	HOMO->L+1 (98%)
			590	HOMO->L+2 (95%)
			562	HOMO-1->L+1 (98%)
			537	HOMO-1->L+3 (84%)
			532	HOMO-1->L+4 (95%)
			518	HOMO-1->L+2 (94%)
PP11	-6.383	-4.041	758	HOMO->LUMO (99%)
			578	HOMO-1->LUMO (97%)
			545	HOMO->L+1 (96%)
			498	HOMO->L+2 (96%)
PP12	-6.370	-4.134	789	HOMO->LUMO (100%)
			565	HOMO->L+1 (98%)
			506	HOMO->L+2 (94%)
				HOMO-1->L+3 (3%)
			505	HOMO-1->LUMO (96%)
			482	HOMO->L+3 (94%)
				HOMO-1->L+2 (3%)
PP13	-6.628	-4.592	836	HOMO->LUMO (93%)
				HOMO->L+1 (6%)
			804	HOMO->L+1 (93%)
				HOMO->LUMO (6%)
			598	HOMO->L+2 (93%)
				HOMO->L+3 (3%)
			572	HOMO->L+3 (95%)
				HOMO->L+2 (3%)
			524	HOMO->L+4 (32%)
				HOMO->L+5 (58%)
				HOMO->L+6 (8%)
			522	HOMO->L+4 (60%)
				HOMO->L+5 (36%)
			505	HOMO->L+6 (82%)
PP14	-6.257	-4.097	858	HOMO->LUMO (99%)
			604	HOMO->L+1 (98%)
			545	HOMO->L+2 (95%)
			537	HOMO->L+3 (99%)
			536	HOMO->L+4 (99%)
			506	HOMO->L+5 (95%)
			493	HOMO->L+6 (96%)
			491	HOMO-1->LUMO (94%)
			428	HOMO-2->LUMO (99%)

PP7

PP12

Figure 6. Contour plots of the frontier orbitals of **PP7** and **PP12**.

2.3. Solvatochromism

Solvatochromic properties of the fourteen dyes were examined in twenty-three solvents of different polarities. Over the years, several empirical polarity scales have been proposed, and the Kamlet-Taft's,[83] McRae Suppan's,[84] Kawski-Chamma Viallet's,[85] Dimroth-Reichardt's,[86] Catalan's,[87] Lippert-Mataga's,[88] and Bakhshiev's[89] scales are extensively used. Considering that two ICT bands can be detected in the visible range, solvatochromic studies were carried out while considering the ICT band located at the lowest energy. A summary of the optical properties is provided in Tables 5 and 6. Excepted for few solvents, all dyes exhibited a sufficient solubility in order their absorption spectra to be recorded. Intramolecular nature of the charge transfer was demonstrated by successive dilutions, and linear correlations could be established between the absorbance and the concentration, discarding the presence of intermolecular interactions. Interestingly, among the different empirical polarity scales used to examine the solvatochromism in solution, the most suitable scales were undoubtedly the Catalan's and Kamlet-Taft's scales (See Linear regressions in SI). In the case of the Catalan's scale, better correlations were obtained while using the solvent polarity/polarizability (SPP) parameter than the solvent dipolarity (SdP) one. Indeed, with the SPP parameter, squares of the correlation coefficients (R^2) were higher than that obtained with the SdP parameter. Interestingly, if all non-specific solvent effects are considered in the π^* parameter of the Kamlet-Taft model, conversely, the Catalan solvatochromic model can discriminate between the non-specific solvent effects such as the polarity and the polarizability. With regards to the results obtained while using the SPP and the SdP parameters, it can be concluded that the solvent polarizability is the main factor governing the spectral shifts of **PP1-PP14**. Good correlation coefficients (R^2) were notably obtained with **PP7** (See Figure 7) irrespective of the solvatochromic scales. However, it has to be noticed that if good correlations were obtained with the two models for **PP1-PP11**, **PP13-PP14**, surprisingly, no trend could be concluded for **PP12**. Indeed, if a clear positive solvatochromism was found for the other dyes, a negative solvatochromism could be established with the Catalan scale for this dye. This irregular behavior can be assigned to the low

solubility of **PP12** in most of the solvents examined, but also to the strong tendency of pyrene to dimerize so that presence of dimers in solution cannot be excluded. Therefore, coexistence of isolated molecules and dimers in solution can drastically affect the optical properties (See Figure 8).

Table 5. Optical properties of **PP1-PP8** in 23 solvents.

compounds	PP1	PP2	PP3	PP4	PP5	PP6	PP7
acetone	491	491	478	472	428	421	596
acetonitrile	491	494	478	466	437	421	603
AcOEt	489	479	469	459	437	431	581
anisole	496	492	474	470	450	446	597
butanol	496	488	479	463	437	437	577
chloroform	497	498	489	472	454	448	596
cyclohexane	486	473	463	449	428	428	574
1,2-dichloroethane	493	500	489	463	454	448	610
dichloromethane	501	498	491	470	444	446	602
diethyl carbonate	484	475	468	472	426	431	561
diethyl ether	486	471	467	456	437	431	578
diglyme	497	485	479	476	428	427	593
1,4-dioxane	482	474	465	459	437	431	567
dimethylacetamide	497	nd	487	469	432	429	604
dimethylformamide	515	505	512	nd	nd	551	616
DMSO	503	504	490	nd	436	433	612
ethanol	506	483	481	nd	420	420	585
heptane	475	468	458	445	424	424	566
nitrobenzene	495	517	503	480	456	449	622
THF	492	486	473	462	437	435	587
toluene	485	481	473	458	439	435	571
triethylamine	539	nd	552	533	518	519	nd
<i>p</i> -xylene	488	479	473	459	440	438	569

nd : not determined. Positions of the absorption maxima are in nm.

Table 6. Optical properties of **PP9-PP14** in 23 solvents.

compounds	PP8	PP9	PP10	PP11	PP12	PP13	PP14
acetone	624	621	679	527	498	557	562
acetonitrile	620	639	681	526	507	556	577
AcOEt	604	608	665	524	497	551	552
anisole	615	641	696	536	516	570	577
butanol	609	625	676	526	508	558	560
chloroform	627	644	697	543	541	588	580
cyclohexane	600	618	nd	nd	528	nd	nd
1,2-dichloroethane	636	654	694	542	528	587	591
dichloromethane	636	636	697	539	528	585	580
diethyl carbonate	587	619	648	514	493	549	547
diethyl ether	592	612	nd	515	nd	557	557
diglyme	617	639	682	527	499	564	562
1,4-dioxane	589	609	nd	513	494	547	541
dimethylacetamide	636	630	696	536	511	568	567
dimethylformamide	647	642	696	542	511	622	569

DMSO	646	642	692	536	516	570	572
ethanol	611	620	676	529	517	nd	567
heptane	593	nd	nd	nd	521	nd	nd
nitrobenzene	660	673	722	549	531	599	592
THF	614	621	676	521	504	561	562
toluene	592	625	667	520	512	557	551
triethylamine	599	607	650	531	511	nd	nd
<i>p</i> -xylene	590	625	662	520	513	557	557

nd : not determined. Positions of the absorption maxima are in nm.

Figure 7. Linear correlations obtained while using two different polarity scales for **PP7** Kamet-Taft a) and Catalan b) and c) empirical scales.

Figure 8. Linear correlations obtained while using two different polarity scales for **PP12** : Kamet-Taft a) and Catalan b) and c) empirical scales.

Slopes obtained by plotting the HOMO-LUMO gaps of **PP1-PP14** vs. the Taft parameters can inform about the electronic redistribution occurring upon excitation of the dyes. As shown in the Figure 9, two different groups of molecules could be distinguished. First, the irregular behavior of **PP12** could be clearly evidenced with its positive slope. Second, **PP2, PP3, PP5, PP7, PP9, PP11, PP13** and **PP14** proved to be the molecules the most sensitive to the solvent polarity but with more pronounced slopes. These dyes also exhibit a similar sensitivity to the solvent polarity, the eight dyes exhibiting parallel slope lines. As a second group, **PP1, PP6, PP8** and **PP10** proved to be less sensitive to the solvent polarity, smaller slopes being determined for these dyes. Based on their chemical structures, no trends could be determined between the fourteen dyes, dyes with electron donors of different strengths being found in the two aforementioned groups.

Figure 9. Top: Variation of the HOMO-LUMO gaps of **PP1-PP14** with the Taft parameters (π^*). Bottom: The two sets of dyes (in violet and black) exhibiting the same sensitivity to the solvent polarities.

2.4. Electrochemical properties

Electrochemical properties of the fourteen dyes examined in this study have been analyzed by cyclic voltammetry (CV) in a dilute solution of acetonitrile. In Figure 10, two curves are provided and all the other CV curves are given in SI. The redox potentials relative to the half-wave oxidation potential of the ferrocene/ferrocenium cation pair are shown for all dyes in the Table 7.

Figure 10. Comparisons between the cyclic voltammograms of **PP7** and **PP9** measured in acetonitrile, with tetrabutylammonium tetrafluoroborate (0.1 M) as the supporting electrolyte, scan rate : 100 mV/s

Table 7. Summary of the electrochemical properties of **PP1-PP14**.

Dye	Reduction (Onset) V/Fc/Fc ⁺	Oxidation (Onset) V/Fc/Fc ⁺	E _{HOMO} (eV)	E _{LUMO} (eV)	ΔE _{ET}
PP1	-0.83	1.06	-5.86	-3.97	1.89
PP2	-0.73	0.98	-5.78	-4.07	1.71
PP3	-0.77	0.93	-5.73	-4.03	1.70
PP4	-0.75	1.01	-5.81	-4.05	1.76
PP5	-0.73	1.08	-5.88	-4.07	1.81
PP6	-0.83	1	-5.8	-3.97	1.83
PP7	-0.73	0.48	-5.28	-4.07	1.21
PP8	-0.83	0.43	-5.23	-3.97	1.26
PP9	-0.76	0.35	-5.15	-4.04	1.11
PP10	-0.78	0.34	-5.14	-4.02	1.12
PP11	-0.77	0.71	-5.51	-4.03	1.48
PP12	-0.68	0.94	-5.74	-4.12	1.62
PP13	-0.7	0.58	-5.38	-4.1	1.28
PP14	-0.7	0.57	-5.37	-4.1	1.27

All potentials recorded in 0.1M TBABF₄/ACN. E_{HOMO} (eV) = - 4.8 - E_{ox} and E_{LUMO} (eV) = - 4.8 - E_{red}

In this study, the fourteen dyes possess the same electron-withdrawing group, but each molecule differs from each other by the nature of the electron-donating groups. As a result of this, major differences can be found concerning their electrochemical properties. Especially, the oxidation potentials proved to significantly differ between the different dyes. For all dyes, similar reduction potentials could be determined, with values ranging from - 0.83 V to - 0.68 V make it possible to demonstrate that the reduction is indeed localized onto the TNF acceptor.

The fourteen dyes could be separated in four distinct groups in light of their electron donating part, with the exception of **PP11** and **PP12** that were prepared with two specific electron donors. In fact, **PP1-PP6** have alkyloxy groups attached to their electron-donating groups, **PP7-PP8** have amino groups in *para*-position of their phenyl rings, and **PP9-PP10** possess the same dialkylamino group in *para*-position

of the phenyl ring. Additionally, an elongation of the π -conjugated spacer between the donor and the acceptor is observed for these two dyes. Finally, **PP13-PP14** comprise a triphenylamine moiety.

Thus, for the **PP1-PP6** series, similar oxidation potentials were determined, ranging from + 1.08 V to + 0.93 V. The lowest oxidation potentials of the alkoxy series were observed for **PP2** and **PP3**, with an oxidation potential located at + 0.98 V and + 0.93 V, respectively. For these dyes, the oxidation process is clearly localized on the alkoxy groups in both the *ortho* and *para*-positions of the phenyl rings of the electron donors.

For the second group and the third group, a decrease of the oxidation potentials was observed so that these dyes showed the lowest oxidation potentials of the series of fourteen dyes. Notably, presence of the electron-donating dialkylamino group in *para*-position of the phenyl ring, but also for the third group of the presence of an extended π -conjugate spacer significantly contribute to reduce the oxidation potential. Indeed, a dialkylamino group is easier to oxidize than an alkoxy group. Consequently, oxidation of the amino group could be detected around + 0.48 V and + 0.43 V for **PP7** and **PP8** respectively. Oxidation at more anodic potentials could be detected for **PP9** and **PP10** at + 0.35 V and + 0.34 V, for due to the elongation of the π -conjugated spacer, better separating the donor from the acceptor. This difference in electrochemical properties can be clearly observed in Figure 11 by comparing the cyclic voltammograms of **PP7** and **PP9**.

For the fourth group composed of triphenylamine-based dyes, oxidation potentials close to that detected for the second group can also be mentioned. This induces that the oxidation process is also localized onto the nitrogen atom of the triphenylam group.

Among this series of dyes, **PP11** and **PP12** differ from the others by their electron donors. Indeed, **PP11** includes a carbazole donor whereas **PP12** comprises a polyaromatic electron donor, namely a pyrene group. In comparison, the oxidation potentials of these two dyes remain lower than those determined for the alkoxy-based dyes but higher than the oxidation potentials determined for the other dialkylamino dyes.

Energy levels of the highest occupied molecular orbitals (HOMO) and the lowest unoccupied molecular orbital (LUMO) of all the dyes could be estimated from their redox potentials and the values are summarized in Table 6. All values have been determined using the ionization potential of ferrocene as the standard (4.8 eV vs vacuum). This correction factor is based on the equations established by Pommerehne et al.[90]

A comparison between the experimental and theoretical values is presented in Figure 11. Good correlations between the two values were found for all dyes. Especially, a better adequation was determined between the experimental and theoretical values of the LUMO levels than for the HOMO ones.

Figure 11. Comparison of frontier orbitals' energy levels obtained from cyclic voltammetry and DFT calculation.

3.4. Thermal properties

Thermal behaviors of the fourteen dyes were examined by thermogravimetric analysis (TGA) measurements. The thermal decomposition temperature (T_d), defined as the temperature at which 5% weight loss of the compound is observed under nitrogen, was determined as being higher than 250°C for all dyes except for **PP9**, **PP12**, **PP13** and **PP14** for which decomposition temperatures around 150°C were found (See Figure 12 and Table 8). Surprisingly, the lowest decomposition temperatures were determined for the triphenylamine and the pyrene-based dyes, with a decrease of the decomposition temperatures of about 100°C compared to the other dyes. At 550°C, the char residue strongly varied between dyes and a residue of 68% for **PP10** to 45% for **PP2** could be determined. Considering the substitution of the different electron-donating groups, no clear explanations could be determined concerning the char residues.

Figure 12. TGA thermograms of **PP1-PP14** measured at a heating rate of 3°C.min⁻¹ under a nitrogen atmosphere.

Table 8. Thermal properties of the push-pull dyes **PP1-PP14**.

	T _{5%} (°C)	T _{10%} (°C)	Char residue at 550°C [%]
PP1	291	306	52
PP2	295	311	45
PP3	242	270	63
PP4	290	303	54
PP5	290	302	53
PP6	267	284	53
PP7	277	282	62
PP8	253	267	60
PP9	143	159	61
PP10	291	295	68
PP11	245	298	63
PP12	133	162	60
PP13	106	147	53
PP14	149	311	65

Conclusion

In this study, fourteen dyes based on the same electron acceptor i.e. tetranitrofluorene (TNF) were synthesized and their photophysical and electrochemical properties analyzed. By changing the electron donor, a shift of the absorption maxima towards the near infrared range was possible. Especially, such a shift could be obtained with strong electron donors such as Michler's aldehyde. Examination of the solvatochromism of the fourteen dyes in 23 solvents of different polarities revealed this solvatochromism to be positive, evidencing the excited state to be more polar than the ground state one. An irregular behavior was determined for the pyrene-based dye, attributable of the low solubility of this dye in most of the common organic solvent, but also to the formation of dimers in solution. Interestingly, TNF constitute an appealing candidate for the design of dyes. First, all dyes can be prepared without taking recourse to a catalytic amount of amine in order the Knoevenagel reaction to proceed and second, these dyes can also be easily prepared by mechanochemistry using a few drops of DMF. Considering that TNF is the only electron acceptor exhibiting a near infrared absorption prior to be connected to an electron donor, future work will consist in designing dyes with more red-shifted absorption, in the 1000-1200 nm range.

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