



Original Research Article

Synthesis and Photophysical Evaluation of Assembly of a New Donor-Spacer-Acceptor (Push-Pull) Molecule

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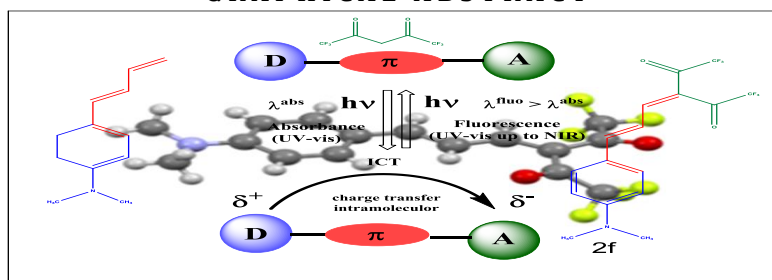
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ABSTRACT

By varying the donor and acceptor groups, which are connected by a π -spacer arm, we designed and synthesised a novel molecule with the donor-spacer-acceptor compound **2f** as a multifunctional component of fluorescence emitters in solution and 93% of yield. The proposed study aims to compare and quantify a set of push-pull type molecules of new linear conjugated systems with a variation of the acceptor force and a distance π between the donor and the acceptor for biological (biomedical) applications and materials in the field of semiconductors and photocatalysis. The absorption spectrums of this molecule, as well as its fluorescence have been studied. Structure **2f** was confirmed by means of single-crystal X-ray diffraction, ¹H-NMR, ¹³C-NMR, ¹⁹F-NMR, and mass spectroscopy. A series of new compounds, similar to a D- π -A, were also designed and synthesised, which show a high propensity for aggregation and crystallization (**2e**, **2g**, and **2h**) and increased the charge mobility in thin films. These push-pull organic molecules are formed from the electron-withdrawing functional groups (diester, diketone, bis-cyano, and hexafluoro-diketone), which are based on useful properties to improve the donor/acceptor interface, the optical absorption in the solution state, and the quantum yield. The photochemical properties of these compounds were studied using UV-Visible spectroscopy and fluorescence. The best dyes with having a yield of 26% (**2g**), 67% (**2e**), and 93% for (**2f**) showed NIR emission in solution state with an emission quantum yield of 14.5% at 627 nm, 1% at 570 nm, and 1% at 621 nm, respectively.

GRAPHICAL ABSTRACT



abstract graphics

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Introduction

Nowadays, many researches are oriented towards the development of a new family of organic molecules as an active medium for solar cells, which are the principal device that converts light energy into the electrical energy through photovoltaic effect [1-3].

A family of molecules, called "push-pull", is particularly interesting because they associate a donor group and an electron acceptor group (donor-spacer-acceptor) [4-9].

The pronounced intermolecular charge transfer (ICT) in the photo-excited state is a favorable criterion for the injection of charge into the photovoltaic cell. In solution, two opposing phenomena can strongly influence this molecular process, while a polar medium favors charge separation; the salvation reduces the energy excess of the excited state and facilitates its return to the fundamental state. The present study on the dynamics of a "push-pull" molecule in its excited state under the absorption of light from fluorescence energy [10] allows a better control of these behaviors and opens up a number of design options for these molecules in the fields of materials chemistry (hybrid materials and photovoltaic cells) [11], as well as in biological and biomedical sciences [12-14].

Some of these molecules are much more emissive in solution than in the solid form. However, when organic chromophores have free spinning groups, the non-radiative return by vibrational relaxation is favored and the molecule becomes non-fluorescent [15]. The aggregation or the crystallization of the molecules limits these spins. Therefore, they become very fluorescent and a high yield of photoluminescence and quantum yield is observed. In particular, fluorescence enhancement by aggregation is very important for the applications of the fluorescent molecules that include visible changes in absorption and emission spectra, quantum yield, lifetimes, energy transfer, solvent effects, scattering, complex formation in addition to a variety of environmental parameters and new materials for lighting devices (OLEDs) or photovoltaic [16]

cells (OPVs). All these elements may be easily accessed by steady-state or time-resolved interpretations of the spectral properties of fluorescent molecules.

Materials and Methods

The present work deals with the synthesis of fluorescent molecules and the evaluation of π -conjugated systems as active materials. The first part describes the synthesis of this series of molecules. The second part of the work deals with the analysis of the structure-properties relations of these molecules by comparing a donor group connected to an acceptor group using π -a spacer. Indeed, molecular dyes based on push-pull molecules represent one of the promising classes of molecules for applications in organic electronics such as solar cells. All of these organic molecules selected for this project are 2D molecules. They are in the form of a globally linear structure, composed of three parts such as an electron-donor group D, an electron-attractor group A (Figure 1), and a π -conjugate linkage between these two groups. This is a type of denoted [17] D- π -A. X-ray diffraction as well as absorption and fluorescence spectroscopy results are presented in the last section.

In the present article, we designed, synthesized, purified, and crystallized a new donor- π -acceptor structure molecule 3-3 [4-dimethylamino phenyl-2propen-1ylidene]-1,1,1,5,5,5 hexafluoro-2-4 pentanedione **2f** using a donor- π -spacer-acceptor structure. As a result, we got a set of fluorescent organic molecules. By varying the donor and acceptor groups, which were connected by a π -spacer arm, we obtained products with a strong light absorption. The studied molecules were characterized by absorbance (UV-Vis), fluorescence spectroscopy, NMR (^1H , ^{13}C , and ^{19}F), mass spectrometry, and structural analysis of single crystals by the X-ray diffraction.

Several series of a set of push-pull organic molecules based on the D- π -A structure with different electron donor and acceptor groups were designed [18], and their spectroscopic properties were examined (Figure 2).

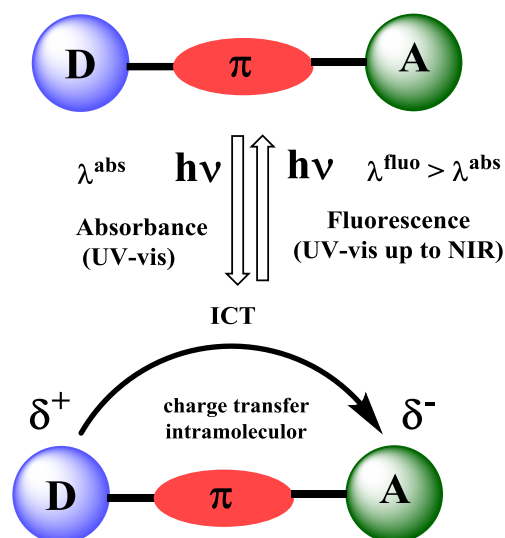
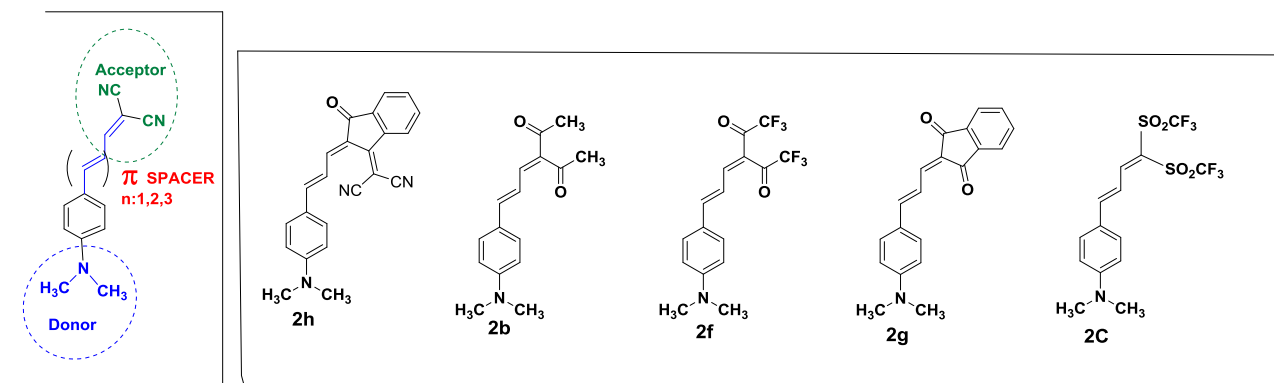


Figure 1: 2D linear push-pull Organic molecule

Figure 2: Different examples of electron-donating groups D, electron-withdrawing groups A, and π -conjugated bonds

It was possible to obtain weak emission in diluted solutions, high emission in the (AIE) [13], and crystalline states. The series of organic molecules selected for the present study is synthesized by the Knoevenagel method [19, 20]. These fluorescent donor-spacer-acceptor molecules contain 4-dimethyl-amino-cinnamaldehyde and cinnamaldehyde as electron donor groups and various electron acceptor groups. The sets of target molecules **2a** [21] **2h** [22] described in Figure 2, could be obtained from dimethyl-amino or a phenyl, respectively. The length of the spacer of 2 double bonds did not change, but a variation of the **2a-2h** series of electron withdrawing substituent such as indanedione, were introduced as acceptors.

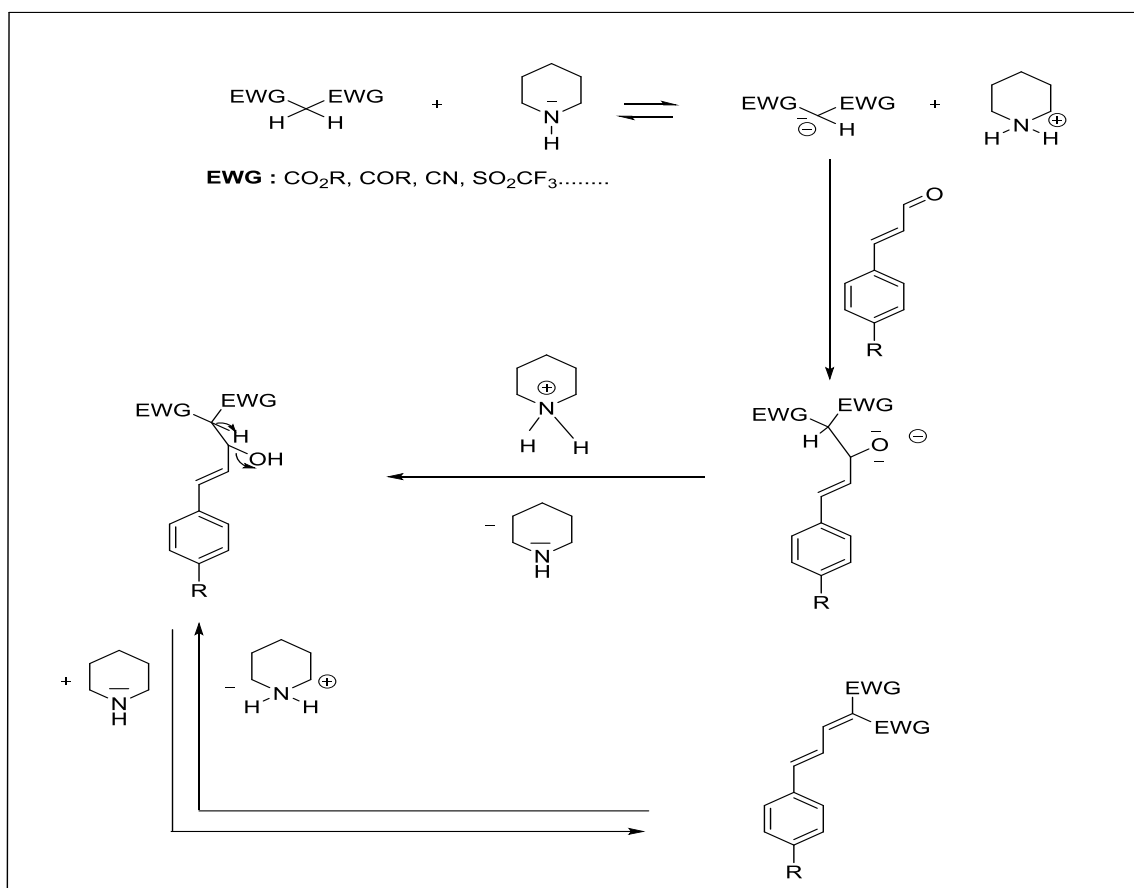
All reagents were used from commercial sources, except the aldehyde (cinnamaldehyde) which

was purified by distillation. The compounds were detected by two superconducting magnet Nuclear Magnetic Resonance spectrometers, a BRUKER Advance III600, and a BRUKER Advance III500. These devices enable the collection of liquid phase high-resolution NMR spectra. The multiplicity of the ^{13}C signals is due to the couplings with the neighboring protons. The quaternary carbon Cq neighboring a single (s), CH doublet (d), CH_2 triplet (t), CH_3 quadruplet (q), and a multiples (m). High resolution hybrid mass spectroscopy coupled with an ultra-performance liquid chromatography (UPLC) chain allows the analysis of complex mixtures, the determination of the exact mass of molecular species in MS, and the fragmentation profile in MS/MS (high resolution on precursor ions and fragments). In addition, a system equipped with Mass Fragment

software was used to assist in the interpretation of spectra and the attribution of fragments. The UV-Visible spectra and fluorescence were registered using a UV-Visible spectrophotometer.

General procedure for synthesis

All the organic molecules selected for the present study were synthesised using the Knoevenagel reaction (Scheme 1), which is an organic chemistry reaction of a methylene compound ($-\text{CH}_2-$) activated by electron-withdrawing groups (EWGs) and an aldehyde within a weak base, removing one molecule of water.



Scheme 1: Knoevenagel Condensation Reaction


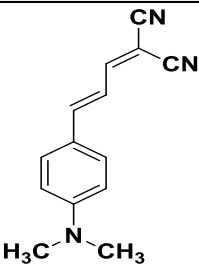
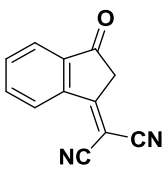
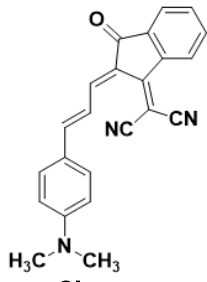
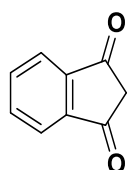
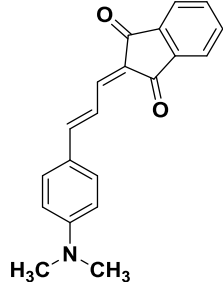
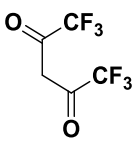
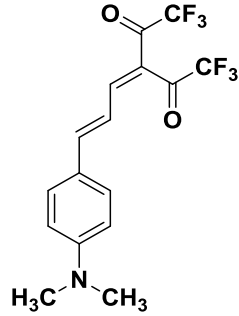
The molecules (**2e**, **2h**, **2g**, and **2f**) were synthesised at various temperatures and solvents with efficiencies of 67% for **2e**, 44% for **2h**, 26% for **2g**, and 96% for **2f** (Table 1), while a piperidine catalyst was present.

In particular, the molecule **2c** with a dimethyl-amino donor group and a fluorinated SO_2CF_3 acceptor group was synthesised within the framework of a collaboration between professors B. Witulski and H. Yannai (Tokyo, Japan) [21]. These molecules were included in our photophysical evaluation, in the solution state.

Synthesis of malononitrile, (dimethyl-amino-cinnamaldehyde) (**2e**)

A solution of 4-dimethyl-amino-cinnamaldehyde (A) (350 mg, 2 mmol) and malononitrile (**7c**) (132 mg, 2 mmol) in ethanol (15 mL) and 2.2 mg of piperazine was added to the mixture. The reaction mixture was stirred at room temperature for 4 hours. The reaction mixture evaporated, and the obtained crystal was filtered and washed by pentane. The product **3** was crystallized with ethanol to give (300 mg, 67% yield).

Table 1: Syntheses of push-pull type organic molecules

	Temperature (°C)	Conditions	Product	Yield (%)
	Room temperature 4 h	Piperazine (2.2 mg) Ethanol (15 mL)	 2e [23]	67 300 mg
	60 18 h	Pyridine (0.016 mL) Ethanol (5 mL)	 2h [22]	44 93.2 mg
	60 3 h	Piperidine (0.01 mL) Ethanol (5 mL)	 2g [24]	26 35.6 mg
	70 18h	Piperidine (0.01 mL) Anhydride acetic (10 mL)	 2f	93 193.5 mg

¹H-NMR (500 MHz, CDCl₃): δ 7.49 (d, *J* = 3 Hz, 1H), 7.47 (s, 2H), 7.17 (d, *J* = 15 Hz, 1H), 7.01 (dd, *J* = 12 Hz, 1H), 6.68 (d, *J* = 9 Hz, 2H), and 3.10 (s, 6H).
¹³C-NMR (125 MHz, CDCl₃): δ 160 (CH), 152.5 (Cq), 151 (CH), 131.1 (CH), 121.6 (Cq), 116.9

(CH), 114.5 (C, CN), 114.5 (Cq), 112.6 (CH), 111.6 (C, CN), and 39.7 (CH₃).

Synthesis of 1,3-indandione, 2-dimethyl-amino-cinnamaldehyde (2g)

A solution of 4-dimethyl-amino-cinnamaldehyde (A) (80 mg, 0.46 mmol) and 1,3-indandione (73.94 mg, 0.506 mmol) in ethanol (5 mL) was analysed in portions with 0.01 mL piperidine and stirred at 60 °C for 3 hours. After cooling at room temperature, the reaction was extracted by DCM. The organic phase was washed with a saturated solution of brine. The product **2g** was isolated after purification by column chromatography by means of DCM/ Ethyl acetate: 98/ 2 as the eluent to obtained (35.6 mg, 26% yield).

¹H-NMR (500 MHz, CDCl₃): δ 8.26 (d, *J* = 12 Hz, 1H), 7.90 (m, 2H), 7.72 (m, 2H), 7.63 (d, *J* = 12 Hz, 1H), 7.58 (d, *J* = 9 Hz, 2H), 7.29 (d, *J* = 14 Hz, 1H), 6.72 (d, *J* = 9 Hz, 2H), and 3.08 (s, 6H). ¹³C-NMR (125 MHz, CDCl₃): δ 191.2 (Cq), 190.8 (Cq), 153.4 (CH), 146.4 (CH), 140.7 (Cq), 134.5 (CH), 134.3 (CH), 131.3 (CH), 124.6 (Cq), 122.6 (CH), 122.4 (CH), 119.6 (CH), 112.3 (CH), and 40.4 (CH₃).

Synthesis of propanedinitrile, 2-3-4-(dimethyl-amino)-phenyl (**2h**)

A solution of 4-dimethyl-amino-cinnamaldehyde (A) (105 mg, 0.6 mmol) and 1-dicyanomethylene-3-indanone (38.84 mg, 0.2 mmol) in ethanol (5 mL) and (0.016 mL, 0.2 mmol) of pyridine was heated for 18 h under reflux. After cooling at room temperature, the mixture was extracted with DCM. The organic phase washed with a saturated solution of brine and dried MgSO₄. The organic phase residue was purified by column chromatography using DCM/Ethyl acetate: 98/2 as the eluent to obtained (93.2 mg, 44% yield).

¹H-NMR (600 MHz, CDCl₃): δ 8.65 (m, 2H), 8.47 (d, *J* = 12 Hz, 1H), 7.83 (m, 1H), 7.68 (dd, *J* = 9 Hz, 2H), 7.60 (d, *J* = 9 Hz, 2H), 7.36 (d, *J* = 15 Hz, 1H), 6.68 (d, *J* = 9 Hz, 2H), and 3.11 (s, 6H). ¹³C-NMR (150 MHz, CDCl₃): δ 189 (Cq), 160.2 (Cq), 156.1 (CH), 153.1 (Cq), 148.9 (CH), 139.9 (Cq), 137.2 (Cq), 134.6 (CH), 133.9 (CH), 132.5 (CH), 125 (CH), 123.3 (CH), 122.4 (Cq), 120.2 (CH), 115.2 (C, CN), 115.1 (C, CN), 112.2 (CH), and 40.3 (CH₃).

Synthesis of 3-3 [4-dimethyl-amino-phenyl-2propen-1ylidene]-1,1,1,5,5,5-hexafluoro-2-4 pentanedione (**2f**)

A solution of 4-dimethyl amino-cinnamaldehyde (A) (100 mg, 0.57 mmol, 0.24 mL) and 1, 1, 1, 5, 5, 5-hexafluoroacetylacetone (**7d**) (142.31 mg, 0.68 mmol, 0.1 mL) in acetic anhydride (10 mL) and 0.01 mL piperidine was heated under reflux for 18 hours. After cooling at room temperature, the reaction mixture was poured into water /ice, and the aqueous suspension was extracted with DCM. The organic phase was washed with a saturated solution of NaHCO₃ and brine, and then it was dried it with MgSO₄. The product was purified by column chromatography (SiO₂) using pentane/ethyl acetate = 8:2 (v/v) as the eluent. After crystallization (chloroform /pentane), (**2f**) was obtained (193.5 mg, 93% yield) as almost red purple solid. R_f = 0.16.

¹H-NMR (600 MHz, CDCl₃): δ 7.74 (d, *J* = 12 Hz, 1H), 7.50 (d, *J* = 9 Hz 2H), 7.36 (d, *J* = 14 Hz, 1H), 7.21 (dd, *J* = 12 Hz, *J* = 14 Hz, 1H), 6.66 (d, *J* = 9 Hz, 2H), 3.10 (s, 6H). ¹³C-NMR (150 MHz, CDCl₃): δ 183.9 (q, *J*_{C,F} = 38 Hz), 178.2 (q, *J*_{C,F} = 35 Hz), 157.4 (br, CH), 156.1 (br, CH), 153.6 (Cq), 132.6 (CH), 122.5 (Cq), 120.6 (Cq), 117.2 (CH), 116.5 (q, *J* = 290 Hz), 115.4 (q, *J* = 290 Hz), 112.0 (CH), and 40.2 (CH₃). ¹⁹F-NMR (470 MHz, CDCl₃): δ 70.8 (s, CF₃), 74.9 (s, CF₃). HRMS (ESI) calc for C₁₆H₁₄F₆NO₂ [M, H]⁺: 366.0929, found Mass: 366.0925.

X-Ray crystal structure of **2f**

Single crystals of buta-1,3-diene **2f** were obtained by crystallization. The dimethyl-amino group and the methylene bonds were situated in the same plane as the phenyl ring and the π-spacer. The carbonyl group was also coplanar with the ring and the π spacer, but the others were out of plane (perpendicular). The molecular structure of **2f** in the single crystal and the molecular assembly are shown in [Figures 3a](#) and [3b](#), respectively.

Results and Discussion

The present study is devoted to the synthesis of different organic molecules of push-pull type which allows presenting the different synthesis routes explored during the present work. Therefore, we presented a synthesis of fluorescent molecules based on the use of

dimethyl-amino, or phenyl, as a donor group among the push-pull molecules of interest for further study. These different compounds were characterized by classical spectroscopic and spectrometric techniques such NMR and HRMS. In the second part, we discussed the physicochemical properties of these series of Push-pull molecules, which are described to evaluate and compare them.

They are dominated by a predominant process of charge transfer from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). Given that the HOMO is frequently centered on the D group and the LUMO is more localized on the A group [25], this is coherent with a charge transfer from the donor D to the acceptor A in the push-pull model of these molecules.

A new molecule (**2f**) was synthesised by coupling 4-dimethyl-amino cinnamaldehyde with 1,1,1,5,5,5-hexa fluoro-2,4-pentanedione. The reaction was promoted under nitrogen and reflux (Scheme 2), resulting in the compound (mass spectra) [C₁₆ H₁₄ N O₂ F₆]. The absorption spectrum of this molecule, the elemental analyses

and ¹H NMR, ¹³C NMR, as well as its fluorescence, were studied. The structure (**2f**) was confirmed using the crystal X-ray diffraction.

Small linear D- π -A systems show greater propensity for aggregation and crystallization. Therefore, they can show better charge mobility in thin films. Examples of some linear push-pull D- π -A molecules are given as follow (Figure 4).

The newly synthesised compounds are illustrated in Scheme 3.

As already mentioned, all the targeted fluorescent molecules were synthesised under reflux and nitrogen, in the presence of good catalysts and common organic solvents. This fact favors any synthetic chemical reaction to obtain the desired pure compounds. We have selected a synthetic route, fixed the donor group, and changed the acceptor group (methylene derivatives). This synthesis technique is simple with good yields. The mixture was deposited at the top of a cylindrical column of stationary phase, where it was adsorbed by forming a disk, and the products can be purified using silica column chromatography [25].

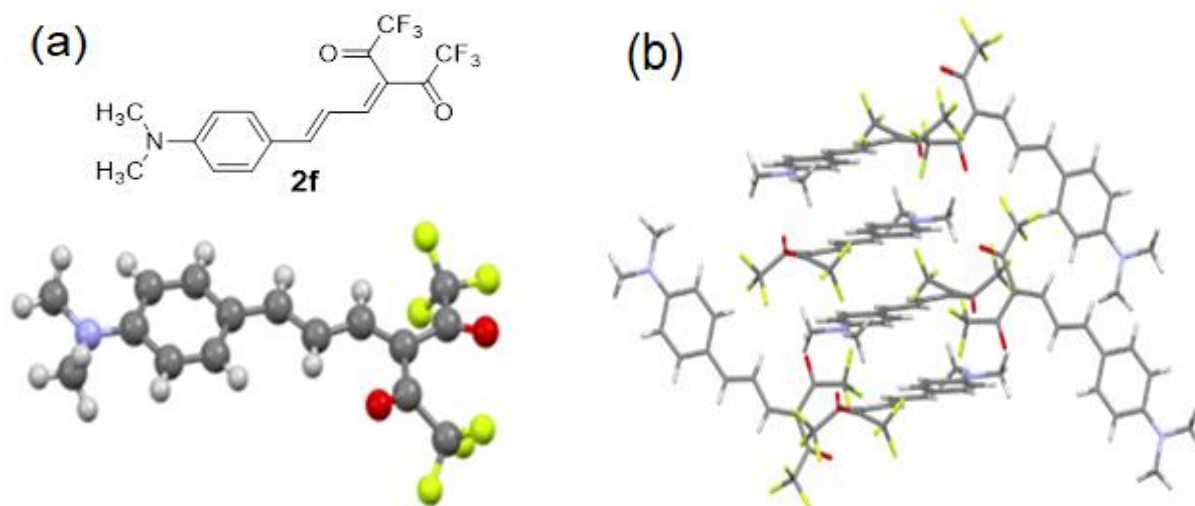
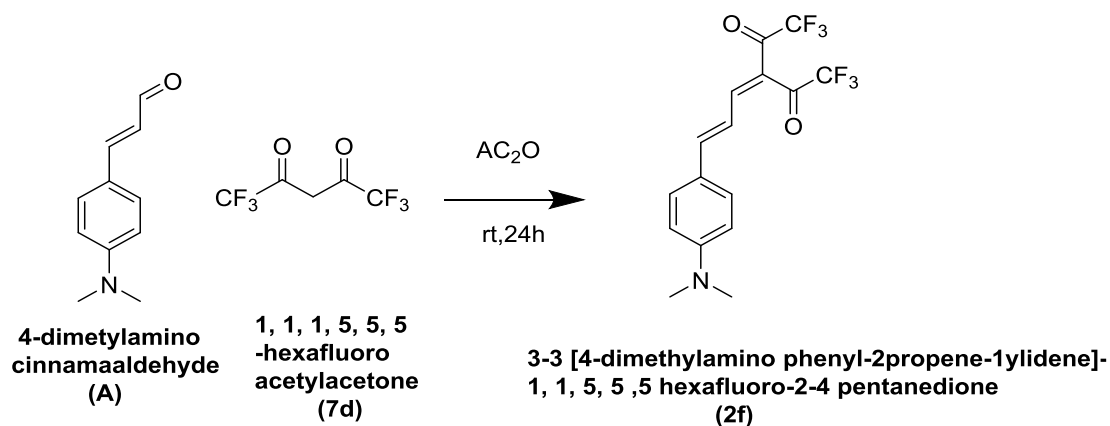


Figure 3: (a) X-ray crystal structure of **2f** and (b) Molecular assembly of **2f** in the monocrystal



Scheme 2: Synthesis of 3-3 [4-dimethyl-amino-phenyl-2propen-1ylidene]-1,1,1,5,5,5-hexafluoro-2-4 pentanedione (2f)

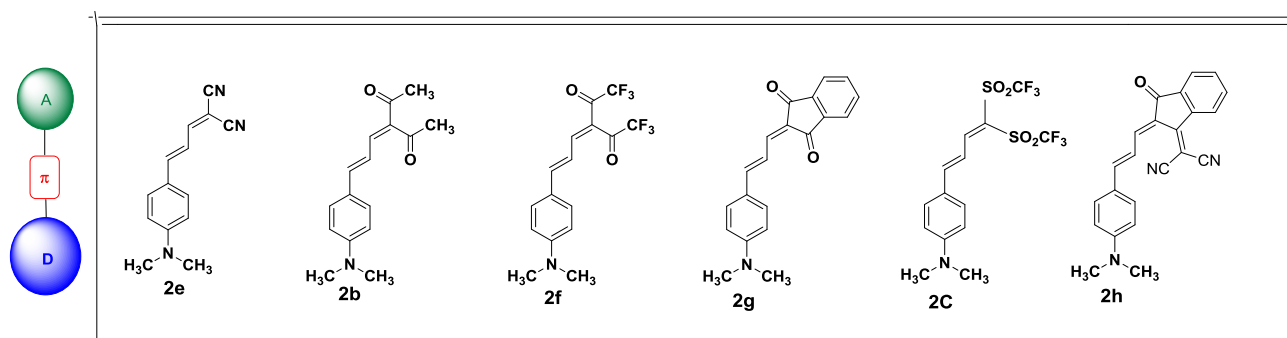
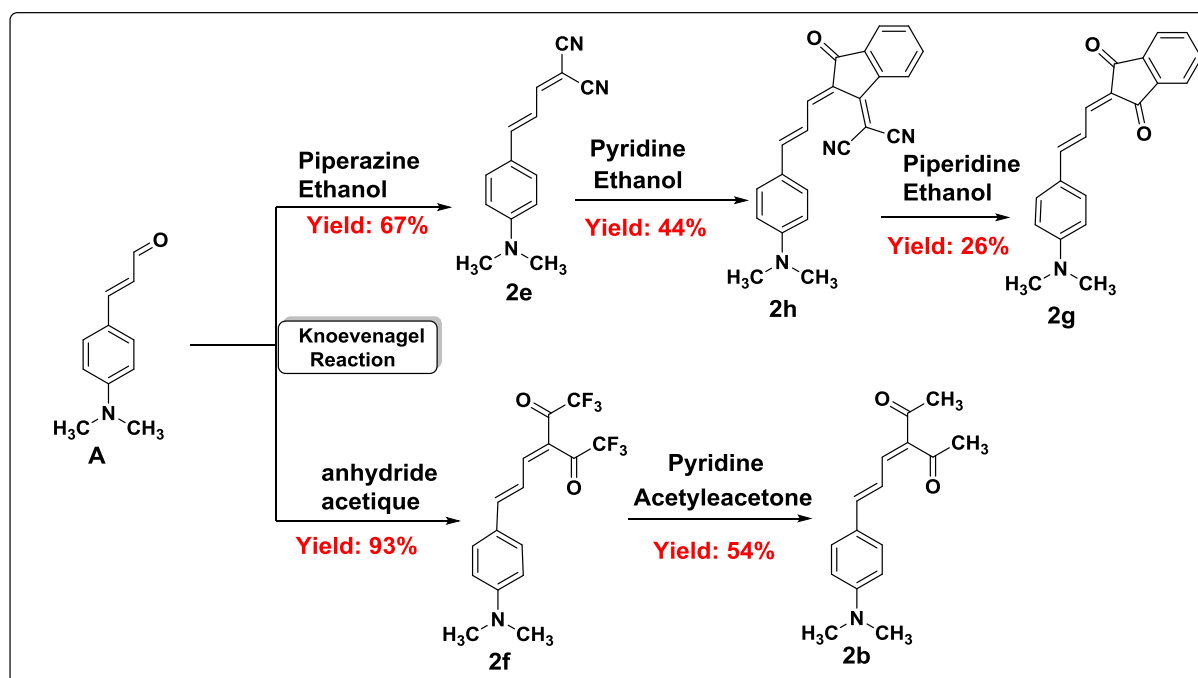


Figure 4: D- π -A linear push-pull molecules



Scheme 3: Knoevenagel reaction and methylene drifts

The second method of purification involved crystallizing solid compounds at a low temperature (in the refrigerator). First, the

minimum amount of CHCl_3 chloroform was introduced to put the solid compound in solution. Next, pentane, was added as a second solvent in

which the molecule was not soluble. Finally, the solution was placed in the freezer for crystallization. It was also tried our crystallization method in this work, using ethanol as solvent for the molecule (**2e**) with a yield of 67% (**2g**) [24] and (**2h**) were prepared by Knoevenagel reaction between aldehyde (A) as donors [26] and the substituent, diketone, indandione, dicyanomethylene-indanone as acceptors with a yield of 54, 26, and 44%, respectively.

Figure 5 depicts the ^1H -NMR, ^{13}C -NMR, and ^{19}F NMR spectra for push-pull molecule **2f** in CDCl_3 .

The analysis of our new molecule using (^1H , ^{13}C , and ^{19}F) NMR signals shows that it has the expected structure. In ^1H -NMR, the three distinctive signals of dimethylamino are discernible as a doublet ($\delta = 7.7$, $J = 12$ Hz), ($\delta = 7.4$, $J = 14$ Hz), and a doublet of doublets ($\delta = 7.21$, $J = 12$ Hz, $J = 14$ Hz), each one is integrating for a proton. The C=C bond in trans is characterized by two doublets ($\delta = 7.50$ and 6.67 ppm) with coupling constant $J = 9$ Hz and integrating for two protons each. Finally, the unit gives an integrating singlet for 6 protons for the benzene ring $\delta = 3.1$ ppm, with a yield of 93%.

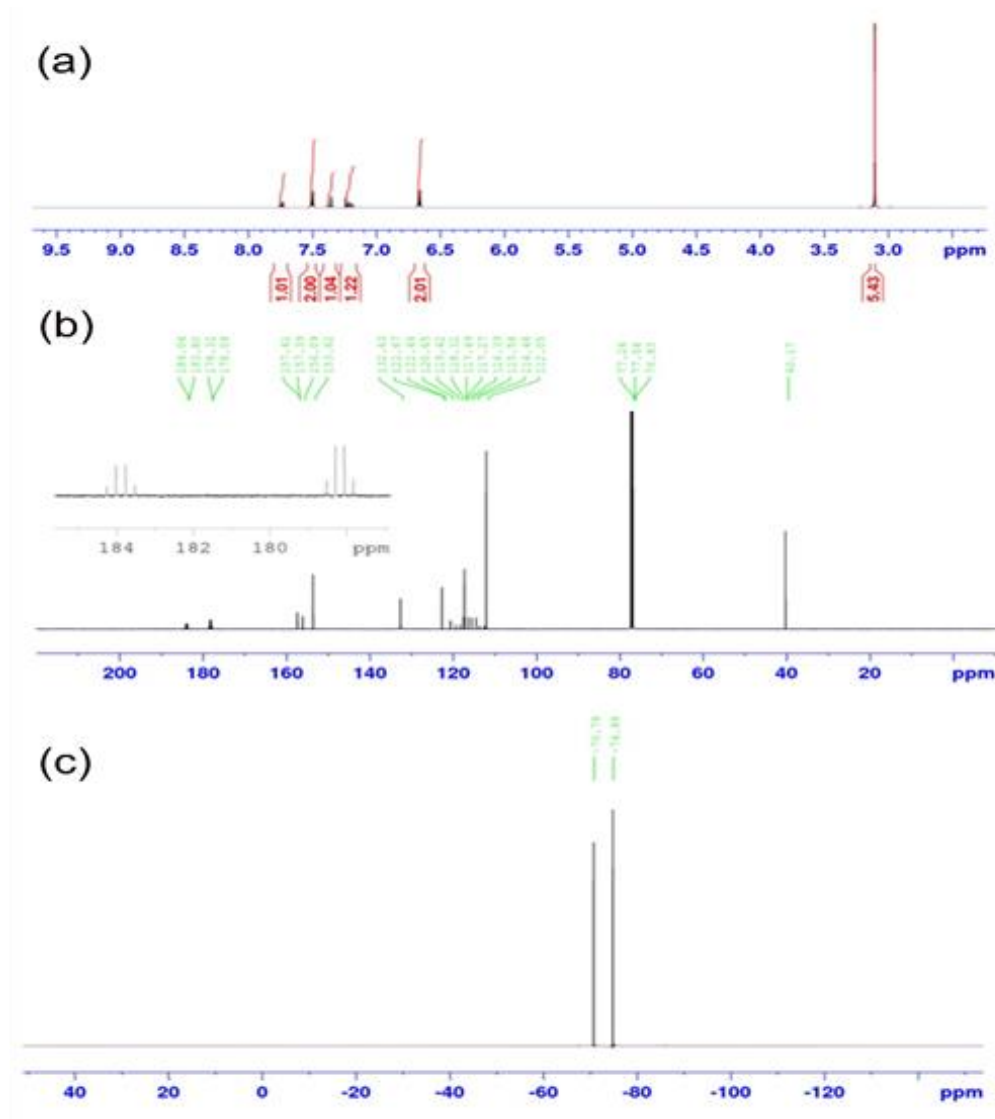


Figure 5: The spectra for push-pull molecule **2f** in CDCl_3 , (a) ^1H -NMR (600 MHz), (b) ^{13}C -NMR (150 MHz), and (c) ^{19}F -NMR (470 MHz)

With the series of new push-pull compounds (**2f**, **2e**, **2c**, and **2g**), the absorption and the emission

maxima in addition to the quantum yields were measured in CH_2Cl_2 (Figure 6a, 6b, 6c, 6d).

The photophysical data are given in Table 2. The spectra in Figure 6 points the charge transfer transitions induced as a function of substituent group strength [27]. In contrast to the compounds **2f**, **2g**, and **2c** [28], of an absorption and emission maxima of 547, 535, and 542, respectively, and emitted fluorescence at 621, 627, and 567 nm, compound **2e** [29] has a substituted group that absorbed light at a shorter wavelength (491 nm) and emitted fluorescence at a longer wavelength (570 nm). Interestingly, the quantum yields of compounds **2f** and **2e** are almost identical. The absorption of methylamino-cinnamaldehyde-substituted hexafluorodiketone and trifluoromethyl sulphonyl was red-shifted. Substitution of the fluoro group with an aldehyde had a significant effect on the photophysical properties as **2f** and **2c**. However, for a given electron donor group, increasing the strength of the electron acceptor caused a red shift in the

absorption maxima: λ_{max} increased from 535 nm for **2g** to 542 nm for **2f** bearing the strongest electron-withdrawing group in (the dimethyl-amino) phenyl series. In all cases, the strongest fluoro electron-accepting group led to the most red-shifted absorption. Upon excitation in the main absorption band, only weak fluorescence was observed for compound **2c**. Compounds **2f**, **2g**, and **2c** displayed emission at 621, 627, and 667 nm (Figure 7a, 7b, 7c, 7d). These emissions are characterized by a Stokes shift ranging between 2190 cm^{-1} for **2f** and 2810 cm^{-1} for **2e**. This later parameter is important to obtain a higher fluorescence yield for biological applications. They are also more red-shifted because of the NIR significance [30] emission for in vivo imaging. Even though the quantum yields low emission, especially for these low molecular weight molecules, such emission wavelengths are interesting.

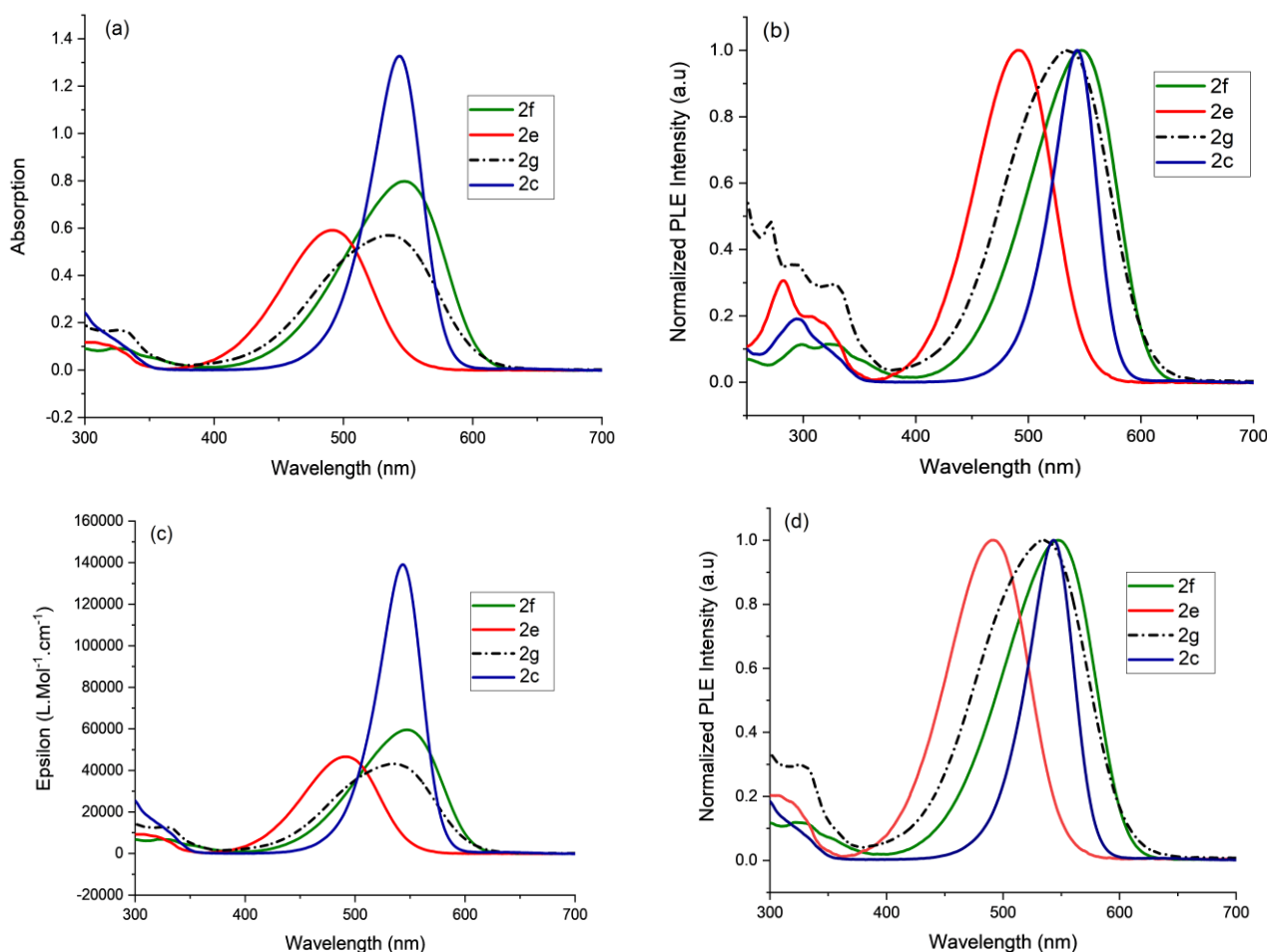
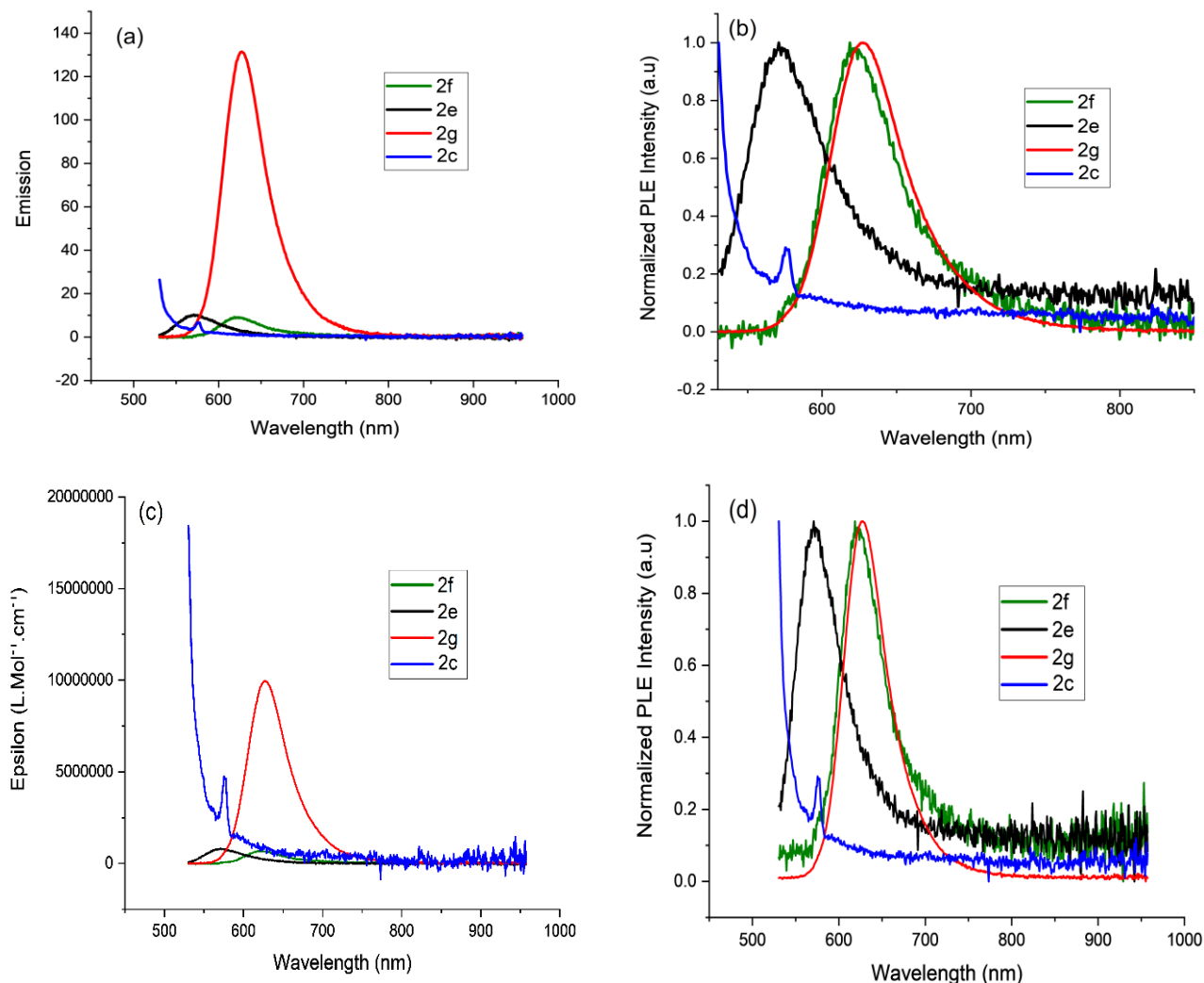


Figure 6: The UV-VIS absorption spectra: **2f**, **2e**, **2g**, and **2c** in CH_2Cl_2

Table 2: Photophysical properties of compounds **2f**, **2e**, **2g**, and **2c** in the solution state

Compounds	Solvent	λ_{Max}^{abs} (nm)	λ_{Max}^F (nm)	Φ_F	Stokes Shift (cm ⁻¹)
2f	CH ₂ Cl ₂	547.55	621.93	0.010	2190
2e	CH ₂ Cl ₂	491.28	570.88	0.010	2840
2g	CH ₂ Cl ₂	535.35	627.37	0.145	2740
2c	CH ₂ Cl ₂	542.95	567.54	-	-

**Figure 7:** Fluorescence spectra of compounds **2f**, **2e**, **2g**, and **2c** in CH₂Cl₂

Conclusion

To sum up, we have demonstrated a very simple and efficient Knoevenagel condensation reaction of cinnamaldehyde, and aldehydes inspired by dimethyl-amino with active methylene compounds, which provides the corresponding substituted electrophiles in different yields and temperatures in a short time of 2 to 24 hours. Utilizing the coupling of 1,1,1,5,5,5-hexafluoro-2,4-pentanedione and 4-dimethyl-amino

cinnamaldehyde, a new donor-spacer-acceptor structure molecule **2f** was created. The structures of the synthesised compounds were verified using ¹H-NMR, ¹³C-NMR, ¹⁹F-NMR, X-ray diffraction, mass spectra, and CHN analysis. These compounds photochemical characteristics were also investigated. The results of our study demonstrated that the **2e** molecule containing a substituted moiety powered the light. These **2f**, **2g**, and **2c** compounds exhibit an emission at 621, 627, and 667 nm, respectively. These emissions

are characterized by a Stokes shift ranging from 2190 cm⁻¹ for **2f** to 2810 cm⁻¹ for **2e**. The later parameter is important for obtaining high fluorescence efficiency for the biological applications. They are also more red-shifted given the importance of NIR emission for *in vivo* imaging. Such emission wavelengths are attractive despite low emission quantum yields, especially for these molecules of low molecular weight. Compound **2e** with a group substitution absorbed light at a shorter wavelength (491 nm) and was fluorescent at a longer wavelength (570 nm) compared with **2f**, **2g** and **2c**, the maxima of absorptions and emission for the three compounds are 547, 535 and 542, and fluoresce at 621, 627, and 567 with quantum efficiency of 0.01, 0.01, and 0.145, respectively.

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Authors' contributions

All authors contributed to data analysis, drafting, and revising of the paper and agreed to be responsible for all the aspects of this work.

Conflict of Interest

There are no conflicts of interest in this study.

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