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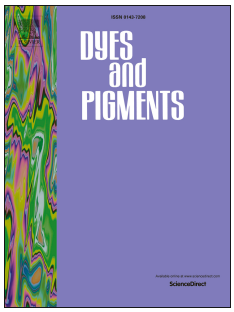

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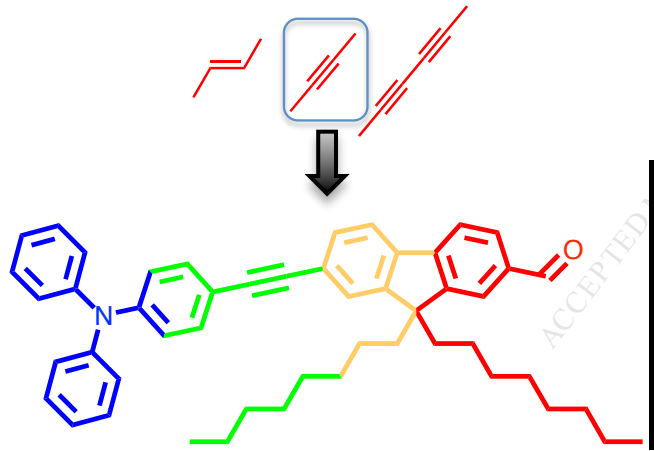

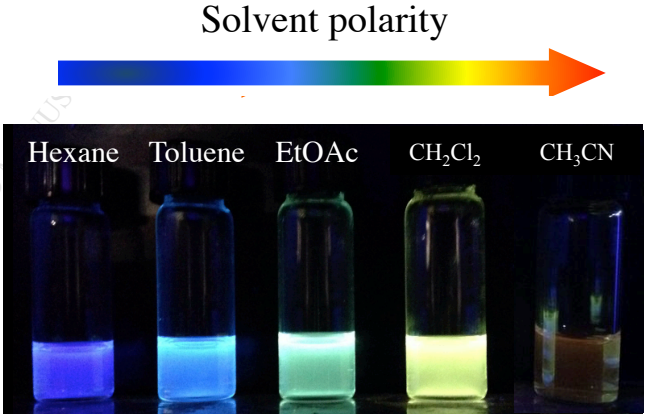

Effect of π-conjugated linkage on photophysical properties: Acetylene linker as the better connection group for highly solvatochromic probes

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Abstract

Fluorophores based in triphenylamine and fluorene (**1-3)** were synthetized and the effects of π-conjugated linkers (vinyl, ethynyl and 1,3-diynyl) on the solvatochromic properties were studied. The fluorescence emission spectra of the dyes were studied using solvents of different polarities, and the influence of specific solvent-solute interactions over emission properties was investigated through Lippert-Mataga model. In particular, we found that compound **2** (with an ethynyl group) exhibits significant advantages over compounds **1** and **3** with vinyl and 1,3-dynyl groups, respectively. It shows a better solvatochromism (140 nm from hexane to CH_3CN), higher Stokes shifts (178 nm in CH_3CN) and more sensitive quantum yields toward solvent polarity (0.09_{DMF}-0.98_{THF}), when compared with those to the reference probe (Prodan). Furthermore, this linker exhibits higher resistance against photodegratation under same conditions. The geometrical and electronic transitions were analyzed by DFT and TD-DFT, and the results are consistent with the experimental observations.

Keywords: *Fluorescence, solvatochromism, Lippert-Mataga model, dipole moment, fluorene derivative, Prodan.*

1. Introduction

Highly solvatochromic fluorescent compounds are widely known to serve as extremely sensitive probes in biological systems for the detection and probing structures[1], lipid quantification[2-4], dynamics[5], micropolarity around a biomolecule[6] and inter-biomolecular interactions[7]. Additionally, they have been used to estimate physical properties as temperature[8], solvent polarity and viscosity[9].

The search for new fluorophores, and particularly environment-sensitive dipolar fluorophores, which change their emission properties in response to variations in their local environment polarity, raised strong interest in recent years[10-14]. Despite large number of solvatochromic dyes already developed[15-18], none of these dyes meet simultaneously all of the spectroscopic requirements for biological applications: absorption in the visible, high absorption coefficient, high fluorescence quantum yield and photostability, as well as strong solvatochromism.

Most of the environment-sensitive dyes exhibit strong changes in dipole moment upon electronic excitation due to intramolecular charge transfer from an electron-donor to an electron-acceptor group; this has allowed the implementation of donor-acceptor model in order to develop a variety of solvatochromic probes[11, 19-21].

Fluorene derivatives have been used in different optoelectronics applications which include organic light emitting devices (OLED's)[22], organic field effect transistors (OFET's)[23], organic solar cells (OSC)[24-26] and recently, their outstanding solvatochromic properties have been shown.[19, 27, 28] A change in the linkage properties between the donor and the acceptor can control the intramolecular charge transfer[29, 30] and the photovoltaics properties[31] in fluorene-based compounds. Based on these facts, in this work we studied the solvatochromic properties of three pigments (**1**-**3**) with triphenylamine and fluorene linked through vinyl, ethynyl and 1,3-diynyl groups, and a carboxaldehyde group was used as an acceptor, Figure 1. The Lippert-Mataga's model and theoretical calculations in ground and excited states were used to analyze the solvatochromism observed in different solvents.

2. Results and discussion

2.1. Synthesis

The synthetic routes followed to prepare compounds **1**–**3** are presented in Scheme 1. Compound **1** was prepared using a Horner-Emmons reaction between the triphenylaminephosphonate **4** and 9,9-dioctyl-9*H*-fluorene-2,7-dicarbaldehyde **5** with *t*-BuOK in THF. Compounds **2** and **3** were synthesized via Sonogashira and Glaser couplings, respectively; slightly modifications were introduced to already described methodologies[31] using the adequate starting compounds **6**-**8**.

2.2. Photophysical properties

Absorption spectra were recorded in different aprotic organic solvents and compared to those of the reference compound, 2-propionyl-6-dimethylaminonaphthalene (Prodan), Figure 2. A broad band characterizes the longest wavelength absorption of compounds **1**-**3**, with the maxima appearing around 406, 380 and 378 nm, respectively. These bands can be assigned as intramolecular charge transfer (ICT) bands that are generated due to charge transfer from the donor group (triphenylamine) to the acceptor group (carbaldehyde) via the π-conjugated linker. As it is observed in the absorption spectrum of dyes **1**-**3** the absorption maxima of **1** is red shifted when compared with **2** and **3**, this is probably because both the ethynyl and 1,3-diynyl groups in **2** and **3**, respectively, act slightly as acceptor groups[29, 32] (for instance, while the Hammett constant (σ_p) for vinyl is 0.06, for ethynyl is 0.21)[33], and reduce the ICT process between donor and acceptor in the ground state. The absorption maximum position for all dyes varies poorly with different solvents, while for Prodan; it shifts slightly to the red in more polar solvents (Table 1).

The fluorescence spectra of dyes **1**-**3** and Prodan were studied in air-equilibrated solutions at 298 K. For all dyes, the emission spectra shift dramatically to longer wavelengths as the

polarity of the solvent is increased (Figure 3 and Table 1). Probably an ICT process through the conjugation moiety occurs in the excited state from the electron donor to the electron acceptor group. This transition yields to the formation of an extremely polarizable excited state [D^+-A^-], which increases their dipole moment. Polar solvent shift the emission to lower energy due to stabilization of this dipolar state, as solvent polarity increased this effect became larger, explaining the positive fluorescence solvatochromism observed[34].

Table 1. Spectroscopic properties of dyes **1**–**3** in different solvents.

		1		**2**		**3**		**Prodan**	
Solvent	**$E_T(30)^a$**	**Abs λmax/nm**	**Em λmax/nm (ϕ)^b**	**Abs λmax/nm**	**Em λmax/nm (ϕ)^b**	**Abs λmax/nm**	**Em λmax/nm (ϕ)^b**	**Abs λmax/nm**	**Em λmax/nm (ϕ)^b**
Hexane	31.0	405	442 (0.60)	384	411 (0.78)	378	422 (0.50)	342	390 (0.07)
Toluene	33.9	411	451 (0.58)	388	441 (0.90)	387	442 (0.94)	349	417 (0.53)
Dioxane	36.0	411	450 (0.67)	381	449 (0.57)	383	448 (0.76)	348	424 (0.61)
THF	38.1	406	451(0.94)	378	495 (0.98)	377	498 (0.90)	348	428 (0.70)
AcOEt	37.4	409	456 (0.60)	376	502 (0.70)	381	500 (0.76)	350	429 (0.78)
$CHCl_3$	39.1	409	459 (0.53)	386	517 (0.47)	375	500 (0.09)	362	437 (0.57)
CH_2Cl_2	40.7	411	469 (0.70)	384	532 (0.64)	365	520 (0.70)	354	439 (0.96)
Acetone	42.2	409	481 (0.33)	373	544 (0.24)	389	541 (0.23)	351	444 (0.66)
DMF	43.2	410	490 (0.12)	380	555 (0.09)	382	523 (0.16)	354	450 (0.93)
DMSO	45.1	408	485 (0.20)	381	560 (0.11)	382	540 (0.20)	359	454 (0.74)
CH_3CN	45.6	406	486 (0.24)	378	556 (0.18)	375	525 (0.20)	350	449 (0.75)
ε/$M^{-1}cm^{-1}$ ^{c}		22100		15400		20500		18200	

a) $E_T(30)$ is the polarity index,[35] b) ϕ is the quantum yield of fluorescence and c) Average of extinction coefficient.

In medium and low polarity solvents, the fluorescence quantum yield (QY) of compounds **1**-**3** is relatively high (0.53-0.98). Overall, it is observed that the fluorescence quantum yields markedly decreases while the polarity of the solvent increases, which is a common property of dyes that exhibit large charge separation in their excited state[1, 7, 36]. Particularly, the decrease in QY with polarity is faster for **2** than for **1** and **3**. The strong quenching of dye **2** by highly polar solvents appears as a useful property in a variety of

applications. For instance, this dye will ‘‘turn on’’ their fluorescence upon binding to apolar biological targets, allowing the study of dynamic proteins interactions[7].

The solvent-dependent spectral shifts are most often quantitatively interpreted in terms of a single parameter, one of the most popular being the polarity index $E_T(30)$; a measure of the ionizing power (“polarity”) of a solvent[9, 35]. A linear correlation of the emission band positions of **1**-**3** and Prodan with $E_T(30)$ is observed, Figure 4. Noticeably, the fluorescent dyes **2** and **3** exhibit a much steeper slope than Prodan and dye **1**, providing a stronger solvatochromic response to changes in polarity.

Another relationship commonly used to specify solvatochromism behavior is the Lippert-Mataga correlation[11, 19], this involves plotting the observed Stokes shift (cm^{-1}) as a function of the solvent’s orientation polarizability (Δf), Equation 1. In this equation *h* is Planck's constant, *c* is the speed of light, and *a* is the radius of the cavity in which the fluorophore resides. ν_{Abs} and ν_{Em} are the wavenumbers (cm^{-1}) of the absorption and emission, respectively. The term $(\varepsilon - 1)/(2\varepsilon + 1)$ accounts for the spectral shifts due to both the reorientation of the solvent dipoles and to the redistribution of the electrons in the solvent molecules and the term $(n^2 - 1)/(2n^2 + 1)$ accounts for only the redistribution of electrons. The spectral shifts due to reorientation of the solvent molecules, orientation polarizability (Δf), were obtained from the differences of the latter terms. The transition dipole moments of **1**-**3** and Prodan are estimated from the Figure 5. The values are 8.0, 14.3 and 11.3 D, respectively. Whereas the obtained transition dipole moment for Prodan was 6.6 D, which is in line with the previously reported experimental and theoretical data[19, 37, 38].

$$\nu_{Abs} - \nu_{Em} = \frac{2(\mu_e - \mu_g)\Delta f}{hca^3} \quad \Delta f = \frac{(\varepsilon - 1)}{(2\varepsilon + 1)} - \frac{(n^2 - 1)}{(2n^2 + 1)} \qquad (1)$$

Dyes **2** and **3** exhibit greater solvatochromic behavior in comparison with **1** and Prodan. While for **1** the emission band shifts by 1987 cm^{-1} from hexane to acetonitrile, the corresponding shifts were 7027 and 4860 cm^{-1} for **2** and **3**, respectively. Additionally, the slope of the curves of the emission maximum versus $E_T(30)$ increased in the following

order: **2** > **3** > Prodan > **1**, confirming the increase in solvent sensitivity. Therefore, these differences in solvent sensitivity correlate perfectly with the increase of the dipole moment difference found: **2** > **3** > Prodan > **1**.

The poor solvatochromic behavior of compound **1**, can be explained by a relative strong donor-acceptor interaction in the ground state (ICT band ~ 406 nm), thus limiting larger changes in dipole moment from the ground state to the excited state. In contrast, the dye based in ethynyl linker **2**, where the acetylene moiety limits a good donor-acceptor interaction in the ground state and promotes greater changes in their dipole moments, showed the best solvatochromic properties. On the other hand, the efficiency of the ICT decreases exponentially with increasing length of the linker moiety[39]. Consequently, the poorer solvatochromism observed in **3**, when compared with **2**, can be attributed to an attenuation of electron transfer process in this dye because of a longer donor-acceptor distance, with 17.5 Å in **2** and 20.1 Å in **3** (from geometrical optimization).

The photobleaching characteristics of fluorescent materials are critical to their application as bio-probes. In the present study, the photostability of dyes **1**-**3** was investigated and compared with that of Prodan, Figure 6. After continuous excitation at 365 nm with a xenon lamp (4.0 mW), the normalized fluorescence intensity of dyes **1**, **3** and Prodan decreased to 52, 26 and 28%, respectively. In contrast, after the same period of excitation, the normalized fluorescence intensity of dye **2** still remained at 89% (decreased 11%). These data established that compound **2** is more photostable than **1**, **3** and Prodan.

2.3. Theoretical studies

The geometrical optimizations and the ground electronic states of compounds **1**-**3** were simulated by density functional theory (DFT) using the Gaussian 09 package. The specific DFT methods used include Becke's exchange (B3) functional, in conjunction with Lee-Yang-Parr (LYP) correlation functional, commonly known as the B3LYP method. The basis set used in all calculations was 6-31G (d). In order to reproduce the electronic and geometrical changes following the excitation the Time Dependent-DFT theory was used.

The optimized molecular structures in the ground state (in vacuum) of the dyes **1**–**3** are shown in Figure 7. It is worth noting that the connectors do not have a significant influence on the torsion angle (σ) between the plane of the donor and that of the acceptor, which means that there is a high degree of π-conjugation. The latter suggests good electronic coupling between donor and acceptor moieties, which determines the charge transfer amplitude[40-42].

The changes in the distance (Δd) during the excitation for selected bonds lengths of the compounds investigated reveal that, from the structural point of view, an important electronic reorganization process occurs during photo-excitation. The differences in Δd between excited and ground state in gas-phase are presented in the Figure 8. As expected, the most sensitive part of the molecules, involving donor and acceptor groups, exhibits noticeable differences especially in N-C and C-O bonds. When comparing these structural variations between dyes **1**-**3**, is evident that compound **2** exhibits greater changes in relevant bond distances, suggesting that the electronic reorganization of this compound in the excited state is larger, supporting the experimental observations.

In summary, the magnitude of solvatochromism in **2** is much higher than that of Prodan, FR0 and other reported fluorene derivatives [19, 43-45], and comparable to that of highly solvatochromic hydroxychromones derivatives (F-HC and 7-AHC), Figure 9. Moreover, this compound exhibits superior photostability than Prodan under same conditions. Based on these results, additional work is currently focused on alkyl chains modifications in order to synthetize new solvatochromic peptides to study protein-peptide inter-biomolecular interactions.

3. Conclusions

We synthetized fluorene derivatives having Donor-Acceptor architecture (**1**-**3**), connected through three different π-conjugated linkers. The absorption and the fluorescence properties were recorded in several organic solvents. While the absorption spectra are nearly independent of solvent polarity, the fluorescence spectra exhibit noticeable solvatochromic behavior. The fluorescence studies show that compound **2**, based on the ethinyl linker, has the largest sensitivity of solvent polarity when compared with that based on vinyl or 1,3-diynyl groups, showing that a small charge separation in the ground state induce a better solvatochromic performance. These behavior is attributed to the greater relative changes in their molecular dipole moment upon excitation, found experimentally and supported by theoretical simulations. The combination of outstanding properties in **2** as absorption in visible region, high solvatochromism, photostability, quantum yield dependence of solvent polarity, when compared with the commercial and commonly used probe as Prodan, and the possibility to incorporate anchoring or functional groups in the 9,9-alkyl chains (without electronic alterations) open the windows to potentials future applications of this dye in the design of molecular sensors.

4. Experimental section

Reagents were used as purchased. The starting materials: triphenylaminephosphonate (**4**)[46, 47], 9,9-dioctyl-2-ethynyl-7-carbaldehyde (**7**)[48] and 4-ethynyltriphenylamine (**8**)[49], and compounds **2**[31] and **3**[31] were prepared following literature procedures and showed identical spectroscopic properties to those reported. All solvents were dried according to standard procedures. All air-sensitive reactions were conducted under an argon atmosphere. Melting points were determined on a Buchi Melting Point Apparatus. Absorption studies were performed using a Cary 5000 UV-Vis-NIR spectrometer from Varian using fused Quartz glass cuvettes with a 1 cm optical path. NMR spectra were recorded on a 600 MHz JEOL (^{1}H: 600 MHz, ^{13}C: 125 MHz) spectrometer and 400 MHz Bruker (^{1}H: 400 MHz, ^{13}C: 100 MHz) using partially deutereated solvents as internal standards at 298 K. Coupling constants (*J*) are reported in Hz and chemical shifts (δ) in ppm. Multiplicities are denoted as follows: s = singlet, d = doublet, t = triplet, m = multiplet. Matrix Assisted Laser Desorption Ionization (coupled to a Time-of-Flight

analyzer) experiments (MALDI-TOF) were recorded on a Bruker microFLEX spectrometer with Dithranol as Matrix and a Shimadzu MS-QP 2010 spectrometer and operating at 70 eV. Analytical thin layer chromatography (TLC) was performed using aluminum coated Sorbent technologies 60 UV254 plates.

4.1. (E)-7-(4-(Diphenylamino)styryl)-9,9-dioctyl-9H-fluorene-2-carbaldehyde (1).

A mixture of diethyl-4-(diphenylamino)benzylphosphonate (**4**) 40.0 mg (0.1 mmol), 2,7-diformyl-9,9-dioctylfluorene (**5**) 54.0 mg (0.12 mmol) and *t*-BuOK 20.0 mg (20.00 mmol) in 15 mL of anhydrous THF under argon atmosphere. The resulting mixture was stirred at 90 °C for 5 h, and then was cooled to room temperature, followed by poured into 50 mL water with stirring. The mixture was extracted with CH_2Cl_2 (100 mL), the organic liquid was combined and washed with brine. After dried with anhydrous $MgSO_4$, the solvent was removed and the crude product was purified by column chromatography (silica gel) with Hexane/CH_2Cl_2 (2:1) as eluent to afford the desired product as a green solid, 64%. Mp: 91-92 °C ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 10.09 (s, 1H, CHO), 7.87-7.85 (m, 2H), 7.80 (d, *J* = 7.9 Hz, 1H), 7.74 (d, *J* = 7.9 Hz, 1H), 7.53-7.51 (m, 1H), 7.48 (s, 1H), 7.44-7.41 (m, 2H), 7.30-7.26 (m, 5H), 7.15-7.09 (m, 5H), 7.08-7.02 (m, 4H), 2.10-1.94 (m, 4H), 1.21-0.97 (m, 20H), 0.82-0.79 (m, 6H), 0.71-0.50 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$, 298K) δ: 194.0, 159.3, 155.8, 148.7, 147.0, 145.5, 137.5, 135.8, 133.3, 131.0, 130.4, 129.4, 127.4, 124.4, 123.5, 123.3, 123.1, 121.7, 121.4, 120.0, 118.6, 115.5, 113.4, 55.4, 40.9, 31.5, 29.9, 29.0, 27.1, 25.6, 23.3, 14.1 ppm. MALDI-TOF MS for $C_{50}H_{57}NO$ m/z $[M]^+$ 687.3980 (m/z expected: 687.4440). Elemental analysis, Calculated: C, 87.29; H, 8.35; N, 2.04. Found: C, 87.30; H, 8.25; N, 2.09.

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Effect of π-conjugated linkage on photophysical properties: Acetylene linker as the betterconnection group for highly solvatochromic probes

Figure List

Fig 1. Structures of dyes **1**-**3**.

Fig 2. Normalized emission spectra of a) **1**, b) **2**, c) **3**and d) Prodan in different solvents.

Fig 3. Normalized emission spectra of a) **1**, b) **2**, c) **3**and d) Prodan in different solvents.

Fig 4. Position of the emission maxima of **1** (green square), **2** (blue triangle), **3** (red circle) and Prodan (black star) versus the polarity $E_T(30)$ in aprotic solvents. The slopes of the linear fits (solid lines) are 169, 549, 437, and 179 cm^{-1}, respectively, and r^2 values (goodness of fit) are 0.909, 0.960, 0.973 and 0.980, respectively.

Fig 5. Dependence of the Stokes shifts (Δν) of dyes **1**-**3** and prodan as a function of the Lippert-Mataga parameter (Δ*f*). Results of the linear fits are: dye **1**Δν = 2047 + 6027 * Δf, r^2 = 0.903, dye **2**Δν = 3522 + 16595 *Δf, r^2 = 0.937, dye **3**Δν = 3135 + 14545 * Δf, r^2 = 0.925, Prodan Δν = 3702 + 7819 * Δf, r^2 = 0.820, where the r^2 value represents goodness of fit.

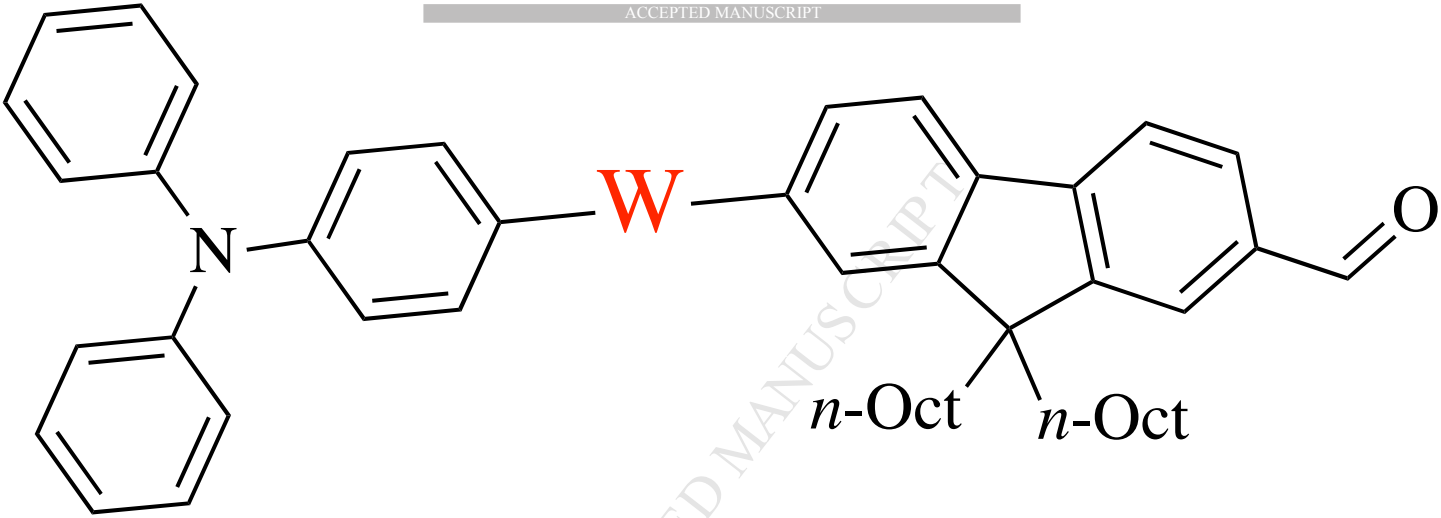
Fig 6. Photostability of dyes **1**-**3** and Prodan in ACN. The fluorescence intensity of dyes was recorded after irradiation at 365 nm (Intensity of the xenon lamp: 4.0 W) for different times. The concentration of the probes was 1 μM. Excitation at 400, 370, 375 and 360 nm for **1**, **2**, **3** and Prodan, respectively.

Fig 7. Optimized structures of dyes **1**-**3** at DFT B3LYP 6-31G (d) level.

Fig 8. Distance changes (Δd) on selected bonds going from ground to excited state for **1** (Red)**, 2** (Blue) and **3** (Black). The geometries were calculated at the B3LYP/6-31G(d) level in the gas-phase. The labeling of bonds is reported in the molecular structures shown on the right.

Fig 9. Comparison of the Stokes shifts and the solvatochromic magnitudes from toluene to acetonitrile of various solvatochromic dyes (**1**-**3**, Prodan, FR0[19], 7-AHC[11] and F-HC[36]),

ordered by the absorption maximum in acetonitrile. The numbers over the bars correspond to Stokes shifts (Black) and solvatochromism (red) in nm.



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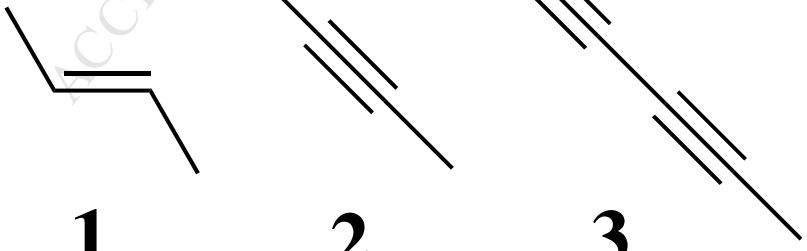
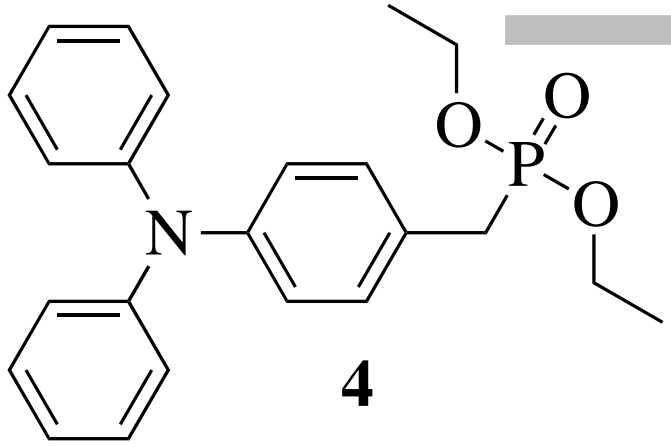


1 2 3



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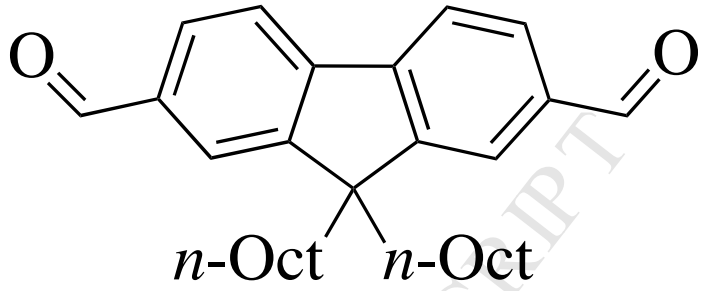
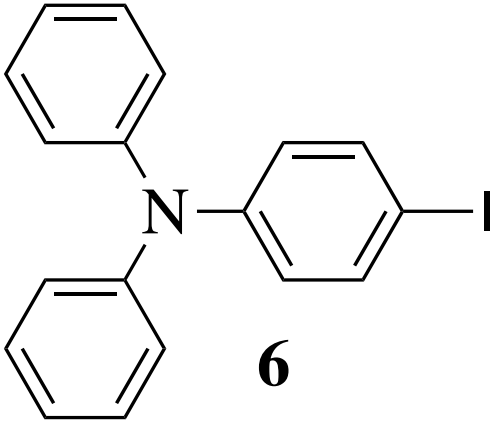


5

$\xrightarrow[\text{THF}]{t\text{-BuOK}}$ **1**



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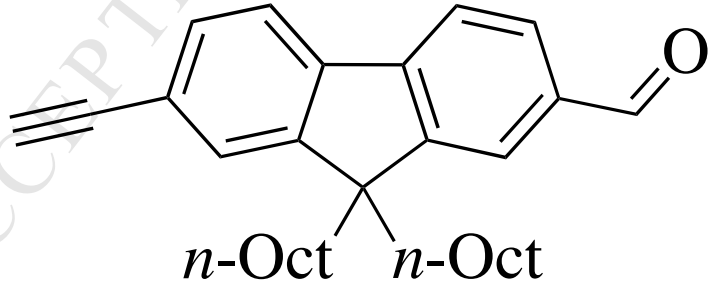
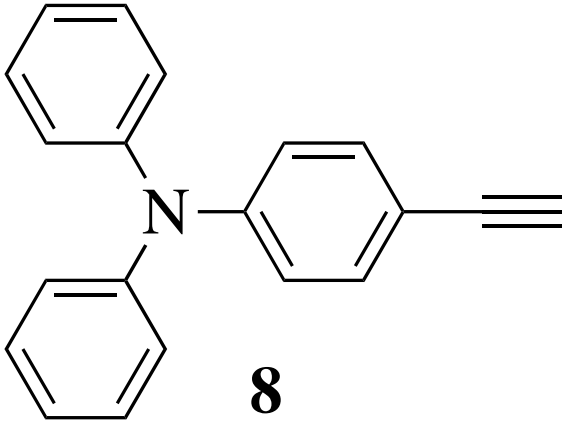


7

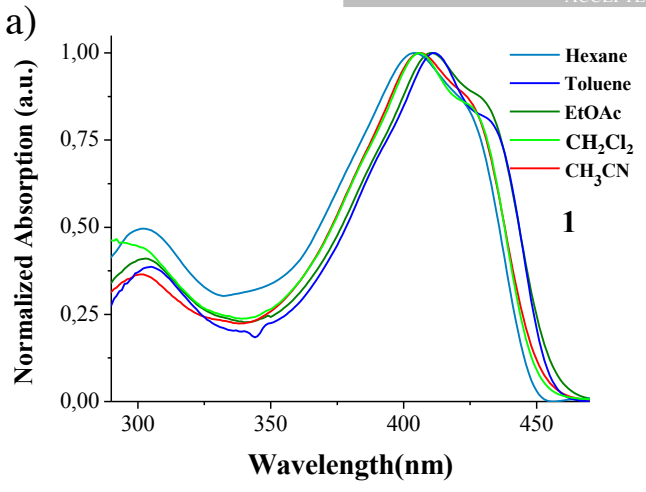
$\xrightarrow[\text{THF}]{Pd_2(dba)_3,\ AsPh_3}$ **2**

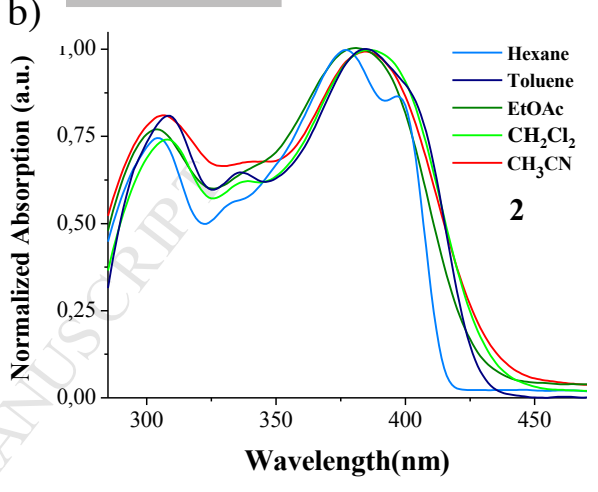


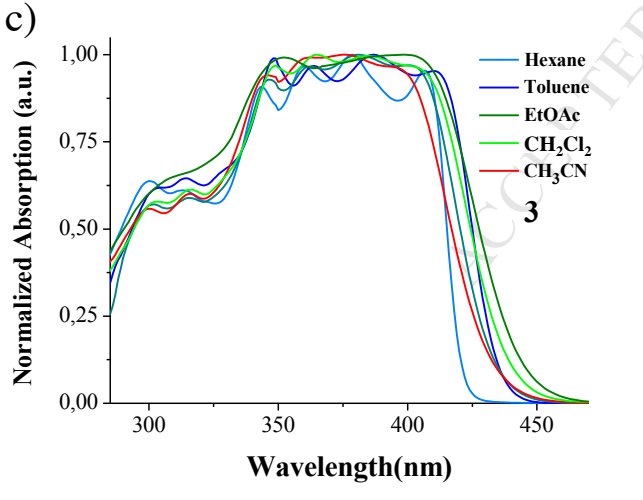
8

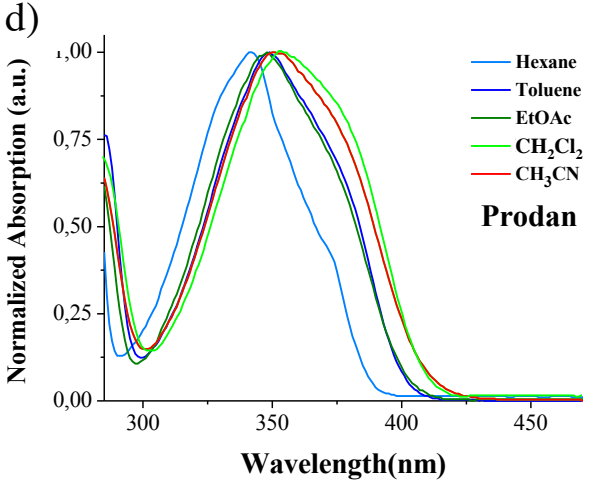
+

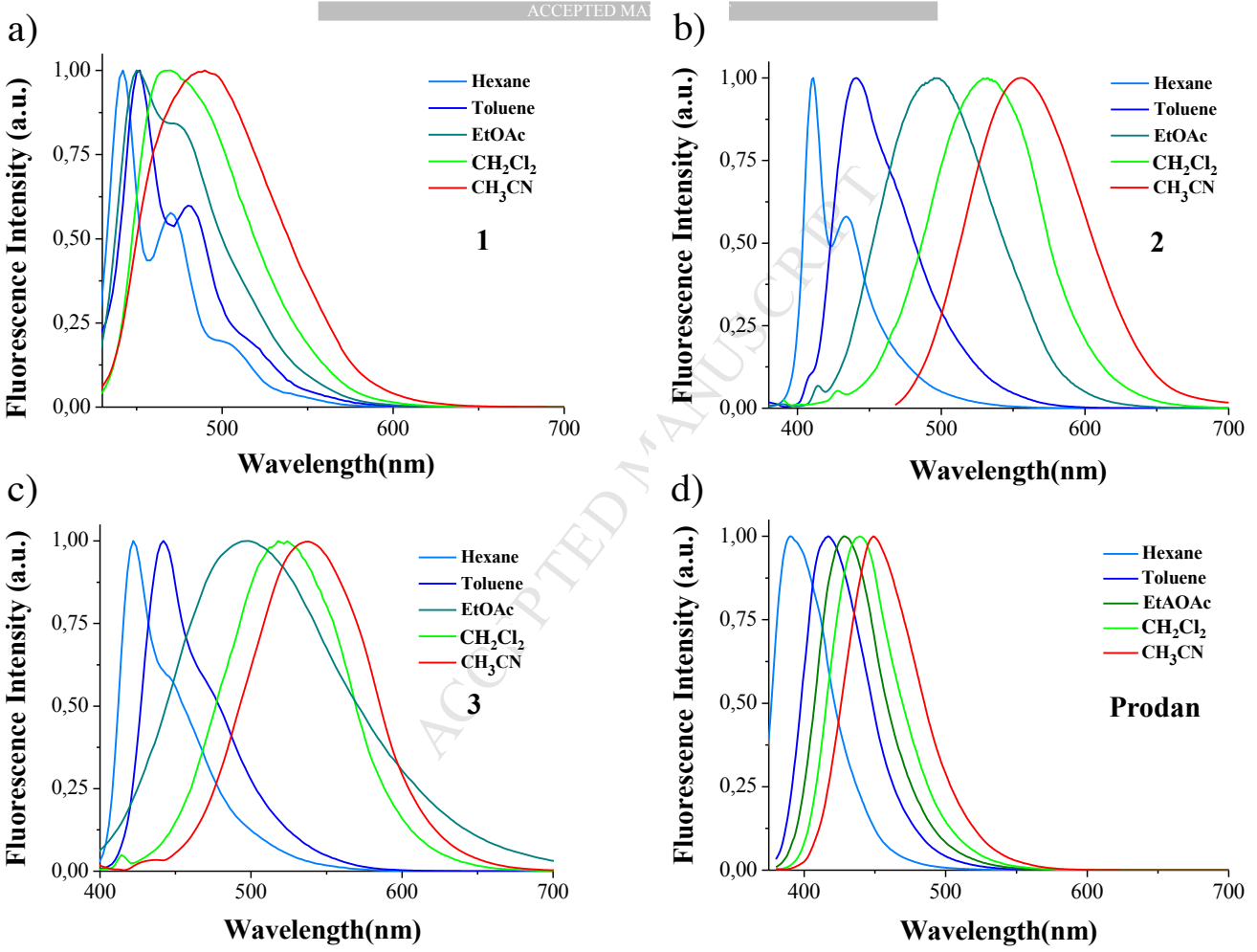
$\xrightarrow[\text{Tol}]{Pd(Cl)_2(PPh)_3,\ CuI,\ I_2,\ TEA}$ **3**

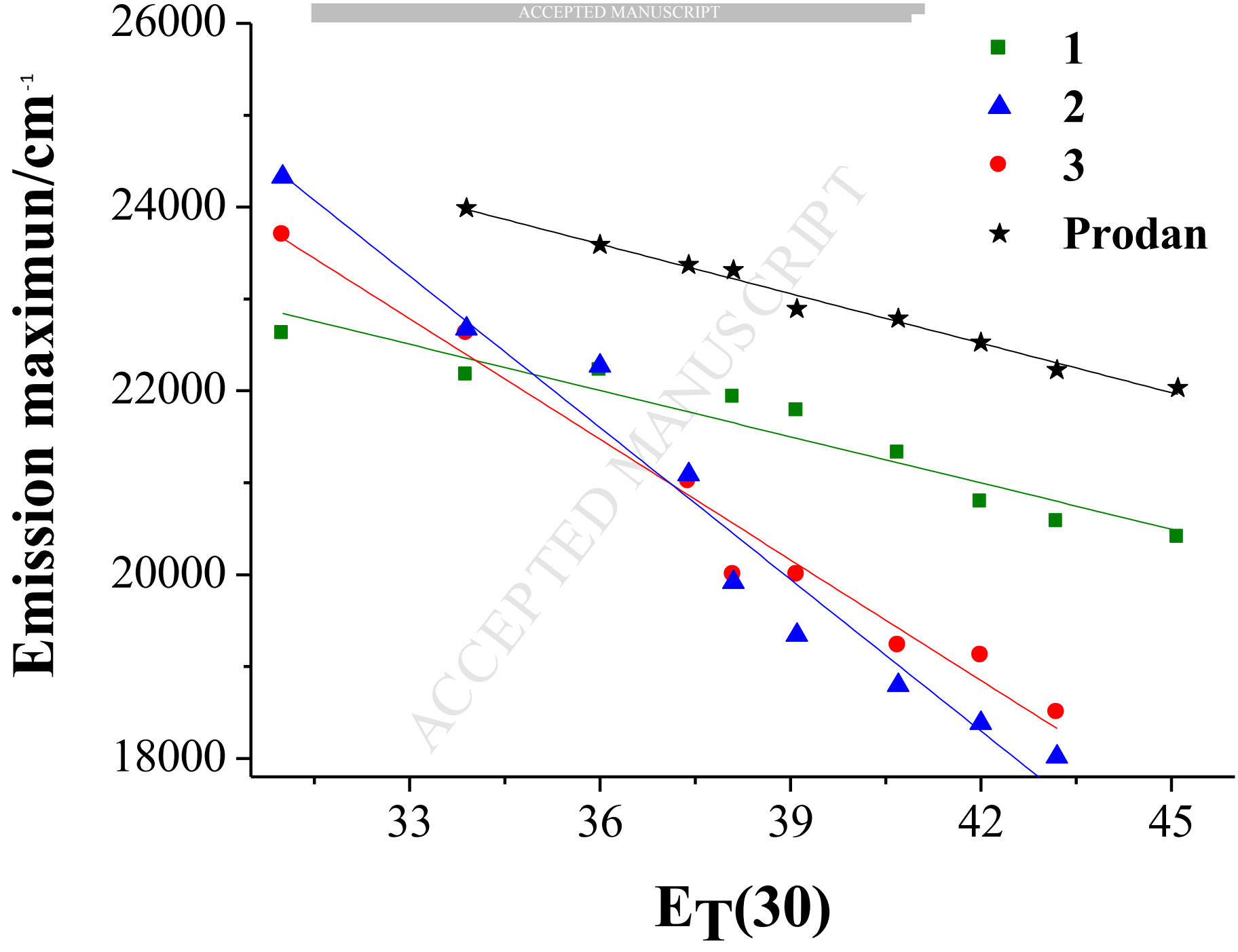


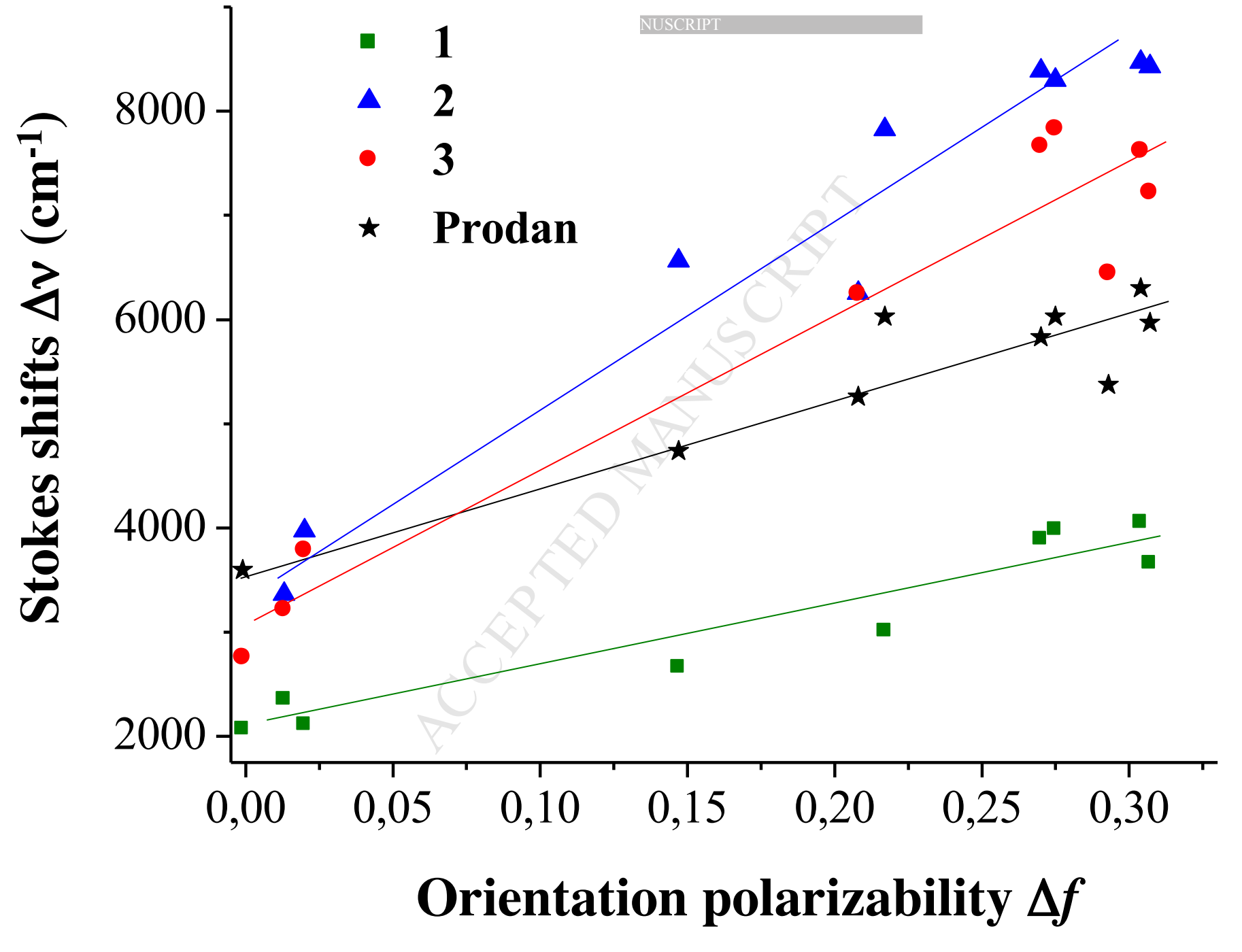


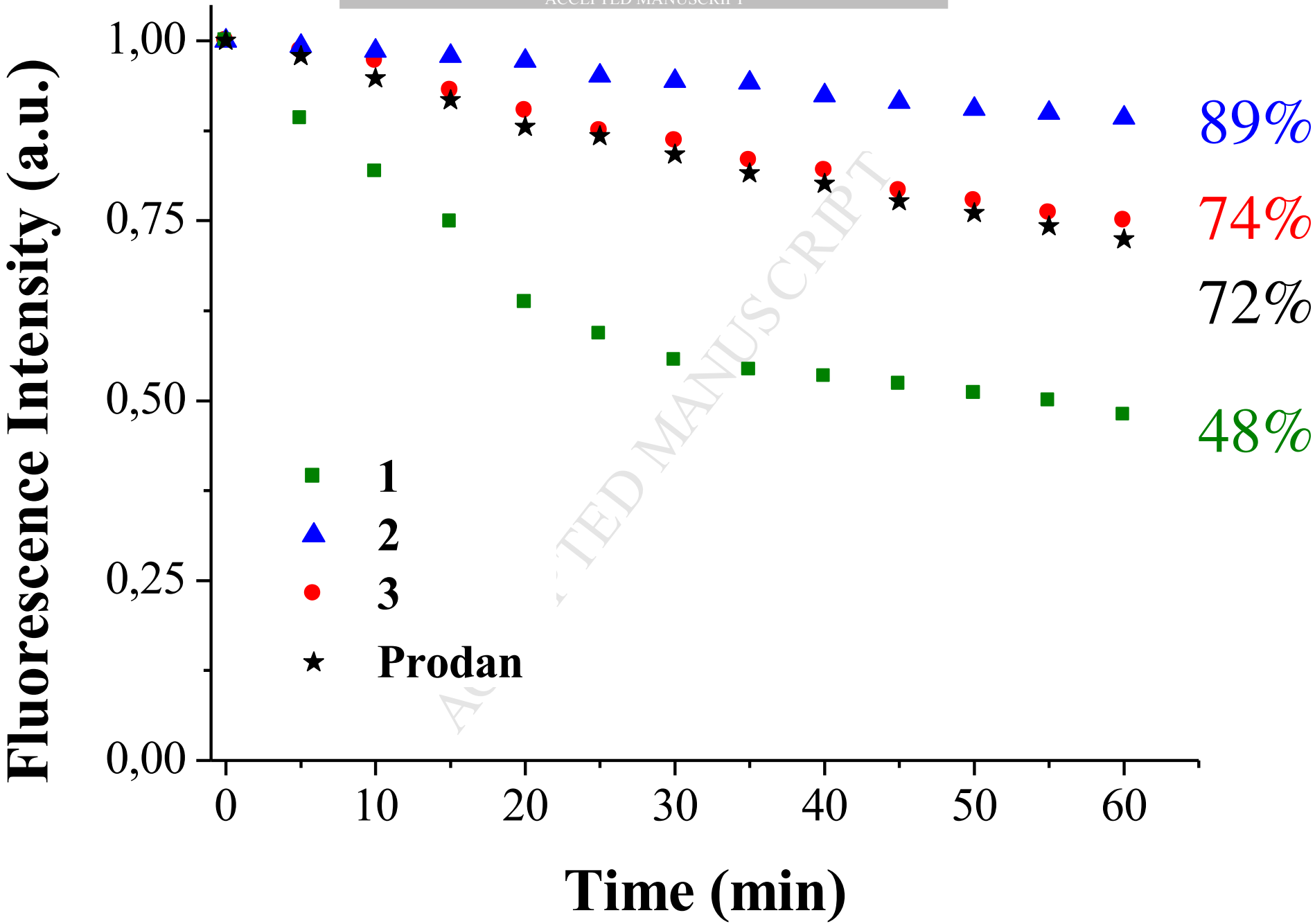


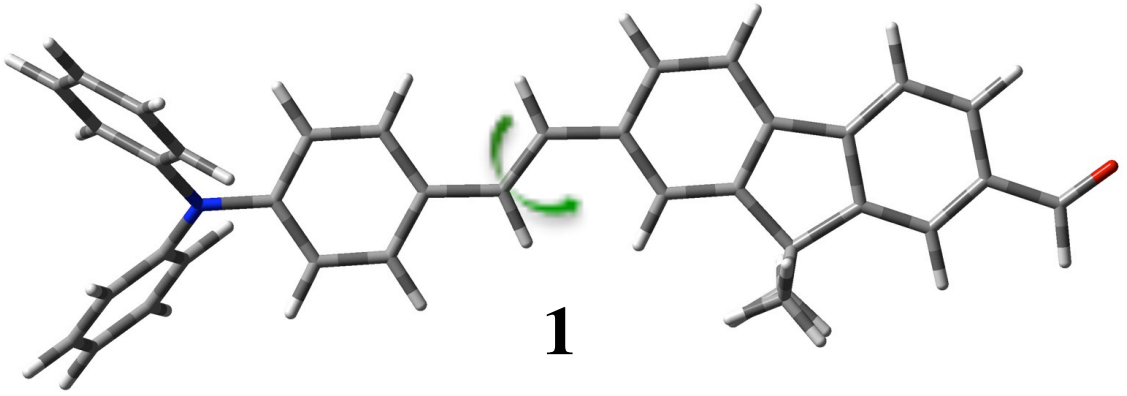







NUSCRIPT
1
2
3
Prodan
8000
6000
4000
2000
Stokes shifts Δν (cm-1)
0,00
0,05
0,10
0,15
0,20
0,25
0,30
Orientation polarizability Δf
ACCEPTED MANUSCRIPT





1

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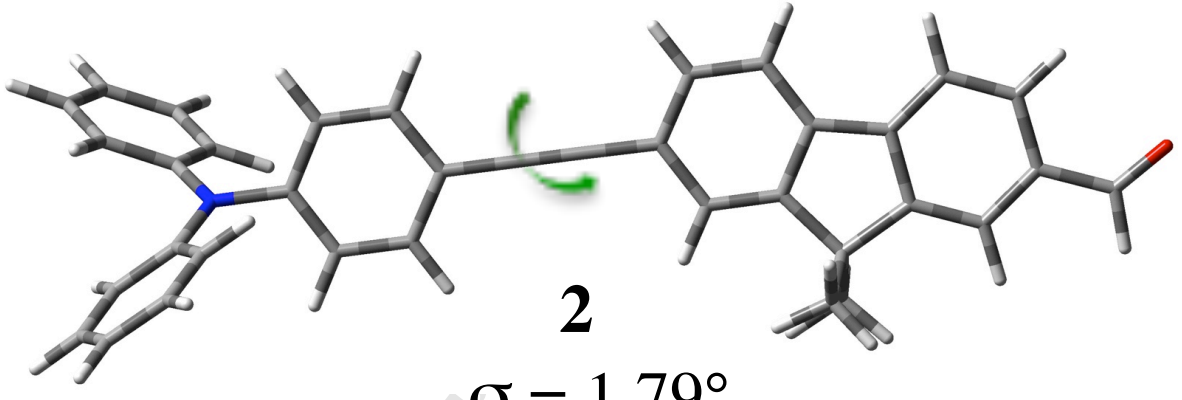

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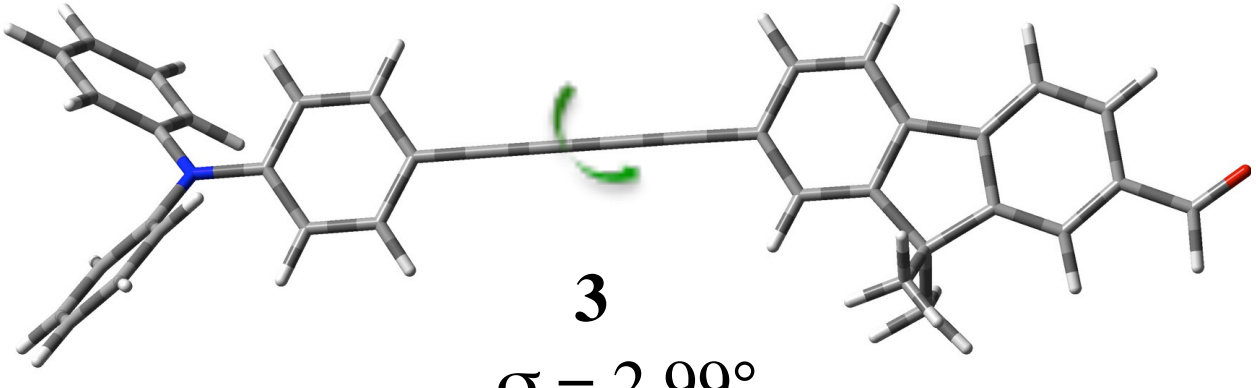
σ = 1.79°



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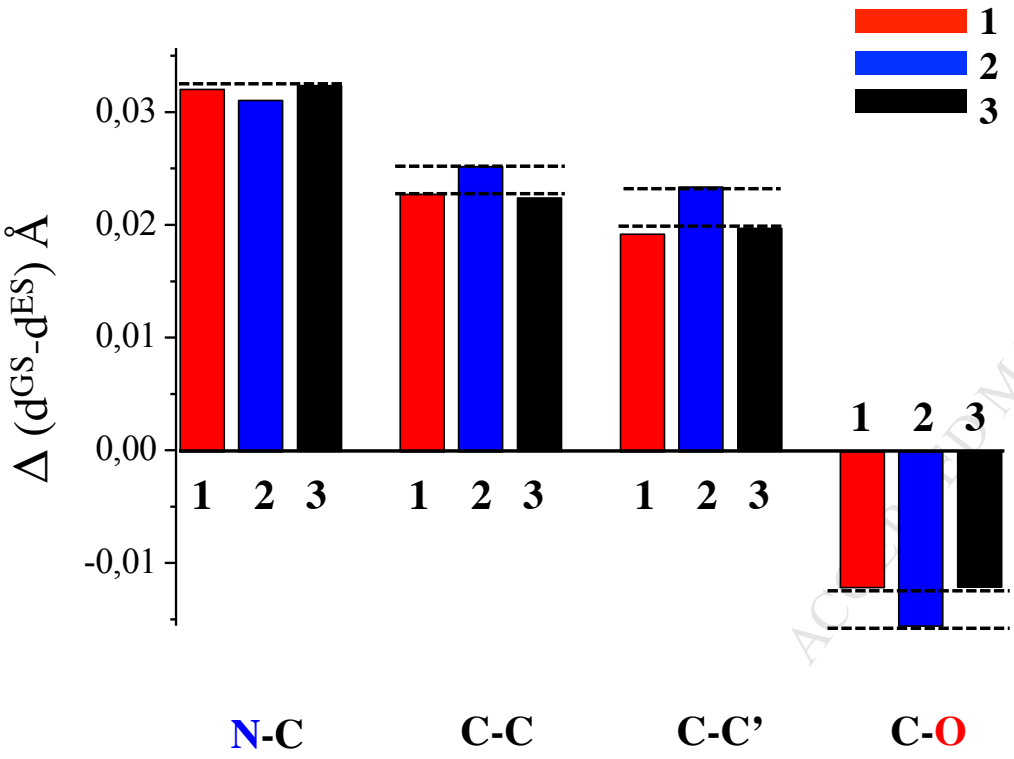
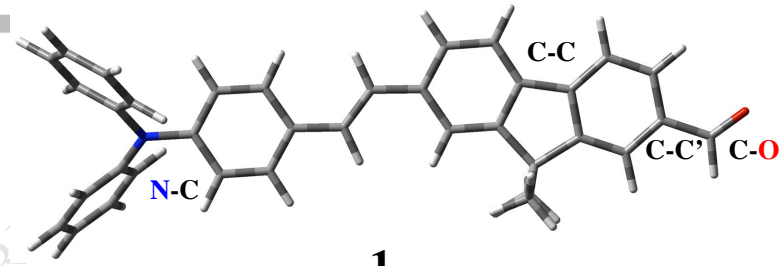
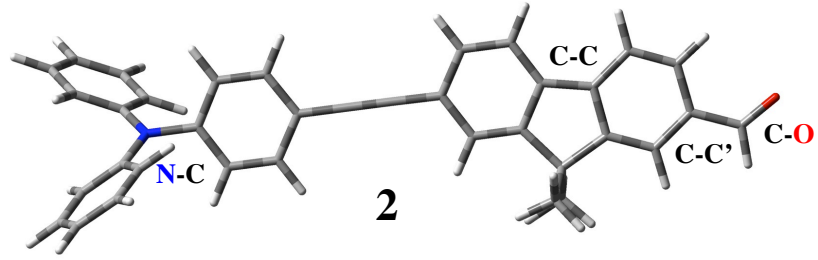
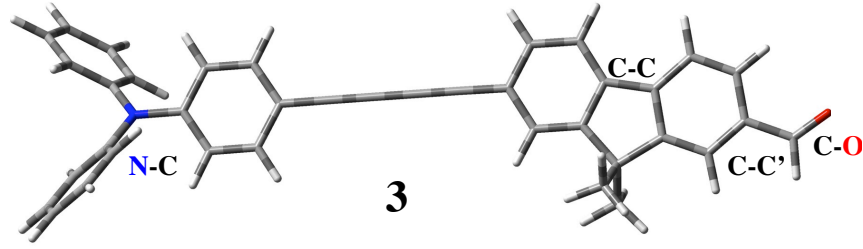
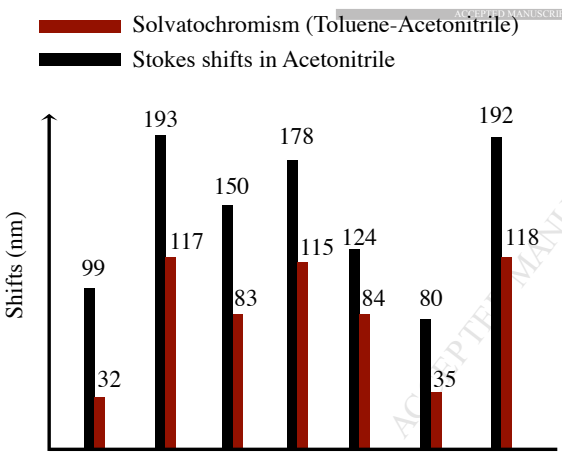
σ = 2.99°



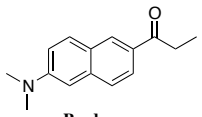


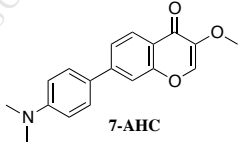


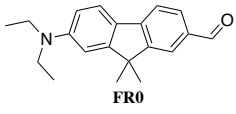


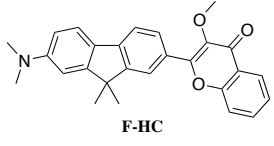


Dye =	Prodan	7-AHC	3	2	FR0	1	F-HC
λ_{max}(nm) =	350	363	375	378	394	406	406









Effect of π-conjugated linkage on photophysical properties: Acetylene linker as the better connection group for highly solvatochromic probes

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Highlights

- The influence of the π-conjugated linker in the solvatochromism was evaluated.
- Acetylene linker improved the solvatochromism, Stokes shifts and photostability.
- The geometrical in the ground and excited state were analyzed by DFT and TD-DFT.