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Push–Pull Amino Succinimidyl Ester Thiophene-Based Fluorescent Dyes: Synthesis and Optical Characterization

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Abstract: The design and synthesis of new fluorescent dyes with emission range at 490–650 nm are described. Their structural and electronic properties have been characterized by both experimental techniques and quantum-chemical calculations. The chromophores are donor–π-bridge–acceptor push–pull compounds with a π bridge of phenyl and thiophene rings and their combination. Compared with previous thiophene fluorophores, these dyes show significant redshift in the absorption and emission spectra and offer compact, red-emitting fluorophores. The dyes have amino succinimidyl active ester and can be readily conjugated to proteins, polymers and other amino-group-containing materials.

Keywords: dyes/pigments · fluorescent probes · oligothiophenes · singlet oxygen · sulfine

Introduction

The analysis of biomolecules and their interaction by means of fluorescent labels is a common technique in today's biological and biochemical research because of its noninvasive nature and its high intrinsic sensitivity.[1] Fluorescence allows qualitative and quantitative determinations and can be performed easily with rapid and inexpensive methodology.

Many fluorescent tags are organic dyes that are also used to trace the presence of biomolecules in cells and other biological systems.[2] Among the reactive dyes, amine-reactive dyes are most often used to prepare various bioconjugates for biological applications since amino groups are either abundant or easily introduced into biomolecules.[2,3] Current organic dyes suffer from many limitations including narrow excitation spectra, broad emission spectra, and photobleaching. On the other hand, our previous papers regarding oligothiophenes as fluorescent dyes encouraged us to further investigate their suitability as fluorophores.[4]

Oligothiophenes are an important class of π-conjugated organic materials that have been investigated as active materials for optoelectronic devices; moreover, they have been employed in photovoltaic solar cells, in light-emitting diodes (LEDs), in photochromic switches, and as field-effect transistors (FETs).[5]

Oligothiophene compounds are chemically stable molecules with a common fluorescent skeleton that can be opportunely functionalized.[6] They display intense absorption bands, the positions of which can be tailored to fall anywhere from the UV to deep-red spectrum by carefully choosing the number of aromatic rings and by introducing suitable substituents at the α positions.[7]

We have recently reported the synthesis of fluorescent thiophene derivatives constituted by an electron-donor (D) and an electron-acceptor (A) group, which interact each other through a π-conjugated spacer. These compounds are characterized by an efficient emission in the blue-orange interval and can be conveniently used to label monoclonal antibodies, toxins, and other amino-group-containing materials.[8]

Donor–π-acceptor fluorescent dyes are characterized by three key components (donor, acceptor, and connecting π system). We report herein on the design, synthesis, and optical characteristics of new fluorescent oligothiophenes with a modified donor group and π bridge.

Results and Discussion

Design and synthesis of oligothiophenes: There is a growing need for cellular imaging fluorescent probes that are able to emit at longer wavelengths and minimize the effects of absorption, autofluorescence, and scattering from biological tissue.[2,3]

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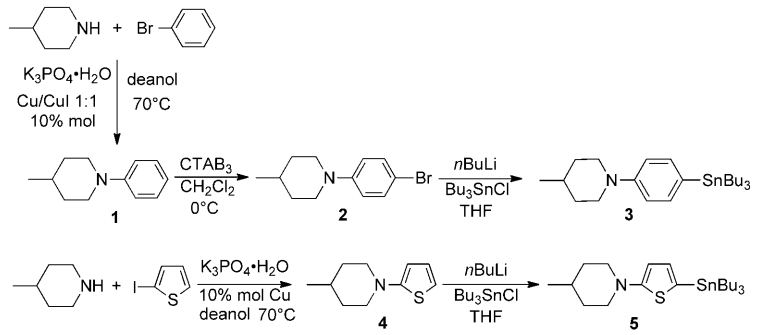
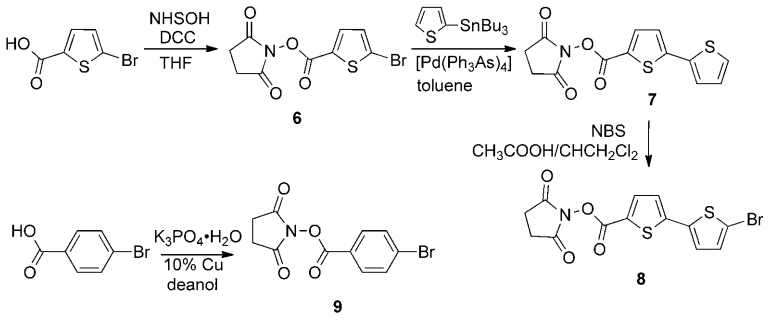
It is commonly known that a shift of the absorption band to longer wavelength in a thiophene-based dye might be obtained by increasing the electron-withdrawing power of the chromophore, by increasing the electron-releasing power of the auxochromes, and by extending the length of conjugation.[9] Furthermore, the thiophene ring not only increases the length of conjugation between donor and acceptor, but also acts as an auxiliary electron donor in push–pull structures.[10] The photochemistry of the thiophene unit has been investigated in a number of thiophene-linked donor–π-bridge–acceptor push–pull chromophores for their optoelectronic properties.[11–16]



Scheme 1. Synthesis of the electron-donor side of chromophores.



Scheme 2. Synthesis of the electron-acceptor side of chromophores.

For this reason, to obtain fluorescent dyes with longer absorption and emission wavelengths, we have chosen 4-methylpiperidine as the donor group, phenyl and/or thienyl rings have been selected for the design of the π-conjugated spacer, and *N*-hydroxysuccinimide (NHS) was chosen to be the acceptor group. Fluorescent dyes rapidly react with primary amines in slightly alkaline conditions (pH 7.2–8.5) to yield stable amide bonds.[17] The labeling reaction completely releases *N*-hydroxysuccinimide within 30 min.

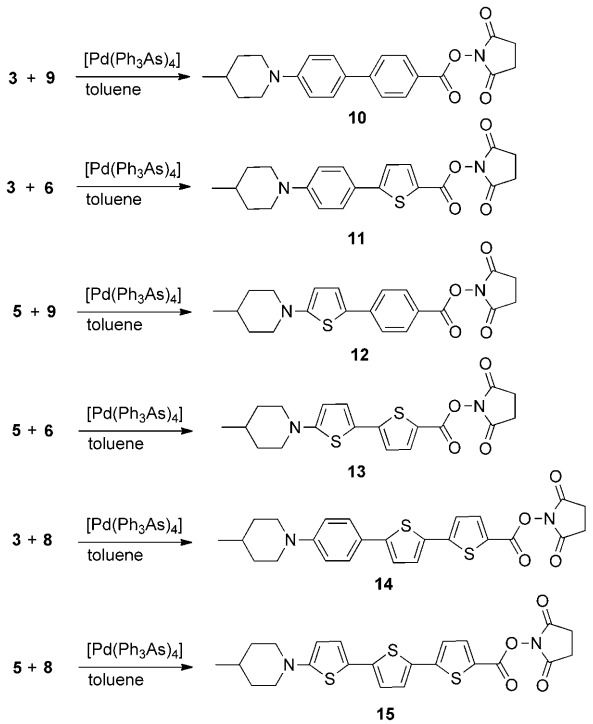
Fluorescent push–pull dyes were assembled in a convergent manner as outlined below. Scheme 1 shows the routes followed to prepare the donor sides of the chromophore, respectively, *N*-piperidinyl phenyl **1** and 2-(*N*-piperidinyl)thiophene **4**. They were synthesized from bromobenzene and 2-iodothiophene by means of a copper-catalyzed amination of the corresponding phenyl or thienyl halogen derivates and by using *N*,*N*-dimethylaminoethanol (deanol) as solvent.[18]

The amination reaction conditions are different for bromide and iodide substrates. For example, for bromobenzene, a mixture of copper metal and CuI is used as the catalyst. Instead, for 2-iodothiophene, only copper metal is employed. Compound **2** was obtained by regio-bromination reaction of 4-methyl-1-phenylpiperidine in aqueous suspension using cetyltrimethylammonium tribromide ($CTAB_3$) as transfer in 98% yield.[19] Stannanes **3** and **5** were obtained in good yields and as pure compound by metalation with *n*BuLi followed by transmetalation with tributyltin chloride.

The acceptor sides of the chromophores were prepared starting from commercial 5-bromo-2-thiophenecarboxylic acid and 4-bromobenzoic acid, respectively (Scheme 2).

Carboxyl groups were converted to *N*-succinimidyl ester by reaction with NHS and dicyclohexylcarbodiimide (DCC) in THF. Compound **6** was further treated with commercial 2-(tributylstannyl)thiophene and subsequently brominated with NBS under dark conditions in a mixture of acetic acid and dichloromethane, thereby affording **8** in 79% yield.

The donor and acceptor precursors were coupled using the Stille palladium-catalyzed cross-coupling to provide the desired chromophores in good yield (Scheme 3). All reac-



Scheme 3. Synthesis of chromophores **10**–**15**.

tions were performed in toluene under nitrogen atmosphere and catalyzed by $[Pd(AsPh_3)_4]$ generated in situ.[20] The chemical structures of all the dyes synthesized for our purpose are reported in Scheme 3.

Optical properties: The normalized absorption and emission spectra of the dyes **10**–**15** have been recorded in CH_2Cl_2 and are shown in Figure 1. These spectra span the UV and visible regions with absorption maxima ranging from 359 to 460 nm, and the spectral shifts are the result of well-known variation in the charge-transfer character of the absorption determined by the nature and the length of the conjugated network.

Excitation of dichloromethane solutions of dyes with a standard laboratory UV lamp ($\lambda_{ex}=365$ nm; Table 1), allowed us to visualize pale green (**10**), deep-green (**11**), green (**12**), yellow (**13**), orange (**14**), and deep-red (**15**) emissions. The bluest absorbing variants of the dyes have a phenyl ring (**10**, **11**, and **14**) attached to the electron donor *N*-piperidine. By replacing the phenyl ring with a thiophene (**12**, **13**, and **15**) the spectra are progressively shifted toward red. Because thiophene has a lower delocalization energy than benzene, it produces better effective conjugation in donor–acceptor compounds relative to benzenoid moieties.[14,21]

The Stokes shift is an important parameter for the fluorescent compounds. Since it provides information on the properties of fluorophores and their structure either at the ground and the first excited state. All new compounds exhibit very large Stokes shifts (difference between the spectral positions of the band maxima of the absorption and emission), from 4363 (**13**) to 7571 cm^{-1} (**10**).

Theoretical calculations: To gain further insight into the effects that different combinations of thienyl and phenyl units have on the effective conjugation of our push–pull chromophores, density functional theory (DFT) calculations were performed on the model compounds **a**–**d** (see Table 2).

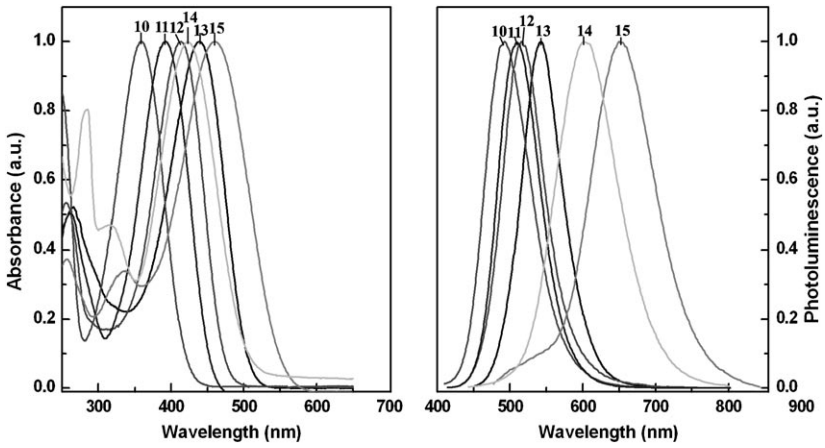


Figure 1. Normalized absorption and photoluminescence spectra of compounds **10**–**15** in CH_2Cl_2. A color version of this figure is available in the Supporting Information.

Table 1. Maximum absorption and photoluminescence wavelengths of compounds **10**–**15** in CH_2Cl_2 and their emission color shown under excitation with a 365 nm UV lamp.

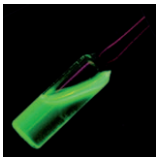
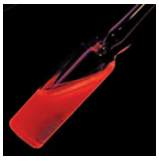
Compound	λ_{max} [nm]	λ_{PL} [nm]	Stokes shift [cm^{-1}]	ε [$M^{-1}cm^{-1}$]	Emission color
10	359	493	7571	16066	
11	393	509	5799	18690	
12	412	515	4854	17194	
13	439	543	4363	17964	
14	422	601	7058	32628	
15	460	650	6497	16685	

Table 2. Selected geometrical parameters and physical properties obtained by the theoretical calculations.[a]

Model compound	ω [°]	d [Å]	$\Delta E_{H\text{-}L}$ [eV]	μ [Debye]	λ_{max} [nm][b]
$(CH_2)_2$N-Th-Th-CHO (**a**)	175	1.438	3.18	7.76	412
$(CH_2)_2$N-Th-Ph-CHO (**b**)	15	1.456	3.37	7.24	360
$(CH_2)_2$N-Ph-Th-CHO (**c**)	23	1.461	3.45	7.24	360
$(CH_2)_2$N-Ph-Ph-CHO (**d**)	33	1.478	3.63	6.89	304

[a] Inter-ring torsion ω [°], inter-ring distance d [Å], HOMO–LUMO energy gap $\Delta E_{H\text{-}L}$ [eV], dipolar moment μ [Debye], absorption wavelength λ_{max} [nm]. [b] ZINDO/S calculations on optimized DFT geometries.

As far as geometrical properties are concerned, it is known that the planarity of the system and the length of the bonds are a good indicator of the overall conjugation. In Table 2, we note an increase of the inter-ring torsion (ω) and of the inter-ring distance (d) going from **a** to **d**, which shows a decrease of the effective conjugation in the same direction. It is interesting to compare these values with the corresponding values for 2,2′-bithiophene (160°, 1.451 Å), 2-phenylthiophene (28°, 1.469 Å), and biphenyl (38°, 1.486 Å) obtained by DFT calculations at the same level. Experimental inter-ring torsions in the gas phase for 2,2′-bithiophene and biphenyl are 148 and 44°, respectively.[22,23] It is evident that the presence of the push–pull groups increases the conjugation in each compound, but this effect is more than marked when more thienyl groups are present. The observed increase of the HOMO–LUMO energy gap going from **a** to **d** is in perfect agreement with a corresponding decrease of the conjugation. In fact, the delocalization energy of thiophene is lower than that of benzene. This behavior is suitably reflected by the values of the physical properties. The color chemistry studies evidenced that the replacement of benzene ring by a less aromatic heterocycle in the π linker in a typical donor–acceptor chromogen determines a significant bathochromic shift of the visible absorption band.[24–26]

ZINDO/S-C.I. calculations show that in all the molecules the UV absorption band is essentially due to a HOMO–LUMO π transition with a charge-transfer (CT) character as shown by the extension of the electronic densities of the frontier orbitals over the entire molecule (Figure 2). It is noteworthy that, in contrast to the geometrical properties, the topology of the alternation of a thienyl with a phenyl group does not seem to strongly affect the physical properties of the system. This signifies that is possible to substitute a thienyl ring with a phenyl ring if necessary without a strong loss of performance.

Detailed discussion of the photochemical reaction of compound 15: During optical measures we observed the decoloration of freshly prepared solution of **15** in dichloromethane under constant irradiation with a UV lamp (λ_{ex} = 365 nm) and the formation of a byproduct (**15a**).

*Structural identification of photoproduct **15a***: High-resolution mass spectrometry indicated that the mass of byproduct **15a** corresponds to the addition of molecular oxygen (HRMS: m/z: 518.0649; see the Supporting Information). A sample of **15a** was generated directly in a NMR spectroscopy tube by irradiating the parent molecule **15** for 2 h with a laboratory UV lamp (λ_{ex} = 365 nm) and was analyzed using NMR spectroscopic experiments.

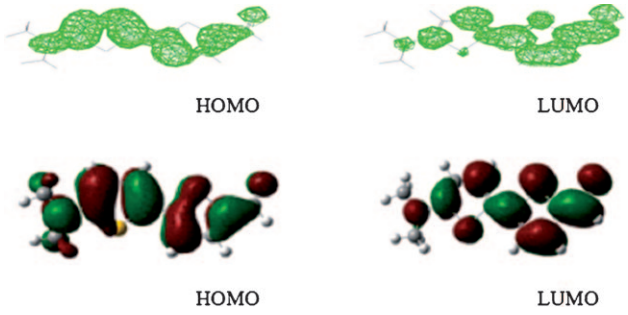
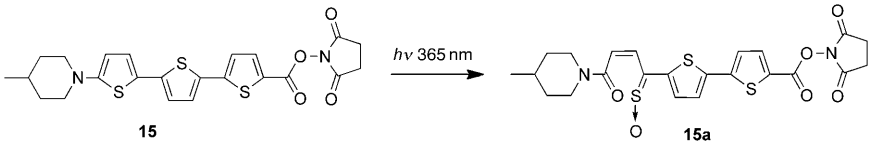


Figure 2. a) ZINDO/S-calculated HOMO and LUMO frontier orbitals of compound **a**. b) DFT-calculated HOMO and LUMO frontier orbitals of compound **a**.

In addition to the signal of two thiophene rings, the ^{1}H NMR spectrum shows two doublets at δ = 6.65 and 7.92 ppm with an unexpected constant coupling J = 10.2 Hz (see the Supporting Information), and a new quaternary carbon at δ = 181.6 ppm is present in the ^{13}C spectrum. To better understand the structure of this byproduct, 2D NMR spectroscopic experiments were acquired. The ^{1}H–^{13}C HSQC spectrum (see the Supporting Information) showed that the two hydrogen atoms at δ = 6.65 and 7.92 ppm are bonded to carbon atoms at δ = 115.8 and 133.6 ppm, respectively. These carbon shifts are typical of an ethylenic system, which would be a *cis*-ethylene, because of the 10.5 Hz coupling. The HSQC spectrum also exhibits four signals that correspond to the CH_2 carbons that belong to the methyl piperidine ring, which are therefore diastereotopic. The ^{1}H–^{13}C heteronuclear multiple bond coherence (HMBC) spectrum shows that the hydrogen at δ = 7.92 ppm is long range coupled with the carbon at δ = 181.6 ppm, whereas the hydrogen at δ = 6.65 ppm is coupled with the quaternary carbon at δ = 164.5 ppm (see the Supporting Information). Finally, an ^{1}H–^{15}N HMBC spectrum (see the Supporting Information) showed that the chemical shift of the nitrogen of piperidine is about δ = 126 ppm, typical of an amidic nitrogen.

All the above data can be rationalized if the sulfine depicted in Scheme 4 is considered, and several data support



Scheme 4. Photooxidation of compound **15**.

this hypothesis: a) the quaternary carbon of sulfine is known[25] to resonate in the range 180–190 ppm; b) the former piperidine nitrogen is now part of an amidic system, and its chemical shift has moved to $\delta = 126$ ppm; c) the carbon atoms of the piperidine systems are diastereotopic because of the hindered rotation about the N–CO bond; d) the resulting *cis*-ethylene system shows the typical *J* coupling of about 10 Hz; e) the conjugation of the oligothiophene is lost and the absorption band has been shifted; and f) the high-resolution mass corresponds to the proposed structure (i.e., to a neat addition of molecular oxygen).

The photosensitizing properties of bithiophene and terthiophene derivatives are known.[28] Moreover, oligothiophenes react with singlet oxygen to give sulfine derivatives with extremely clean reactions.[29]

Labeling: Dyes **14** and **15** were tested for protein and microsphere labeling to investigate their behavior after conjugation.

*Conjugation of terthiophene **15** to saporin*: The plant toxin saporin was conjugated to dye **15** with the same procedure described in our previous paper.[4c] HeLa cells, derived from a human cervical carcinoma, were cultured in Roswell Park Memorial Institute (RPMI) 1640 medium supplemented with 10% fetal calf serum (FCS) and antibiotics. HeLa cells were seeded on four-chambered culture slides (Falcon BD) (5000 cells per well) in complete medium. After 24 h, cells were incubated with 10 μM saporin–**15** for 1 h at 37°C. After treatment, cells were washed twice with phosphate buffer solution (PBS) and then fixed with cold methanol at −20°C for 15 min. Photoluminescence measurements were performed by exciting the solutions at optimum wavelengths for absorbances 0.1–0.2.

After endocytosis of saporin–**15** by HeLa cells, no photobleaching of dye was observed after continuous excitation for 180 s (Figure 3).

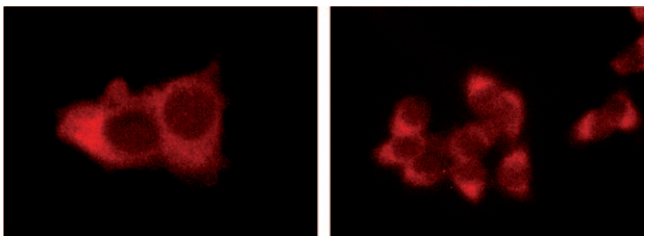


Figure 3. Binding and endocytosis of **15**-labeled saporin by HeLa cells.

*Labeling of dye **14** to polystyrene microspheres*: We used for our study nominally 6.31 μm amino-modified polystyrene microspheres, with about 134 $\mu_{eq}\,g^{-1}$ amino groups attached to the surface of the particles by alkyl chains. The fluorescent dye **14** was covalently bound to microspheres in dry dimethyl sulfoxide (DMSO). The tagged microspheres were separated from unconjugated dye using microfiltration through a 0.45 μm syringe filter and washed with DMSO and Millipore water several times.

The particles were redispersed in PBS buffer and sonicated before examination with fluorescent microscope. As shown in Figure 4, the labeled microspheres–**14** have good photostability under constant illumination with a fluorescent microscope excitation source for 60 s, whereas under the same conditions nearly complete degradation occurred for fluorescein-labeled spheres after only 30 s of exposure.[8]

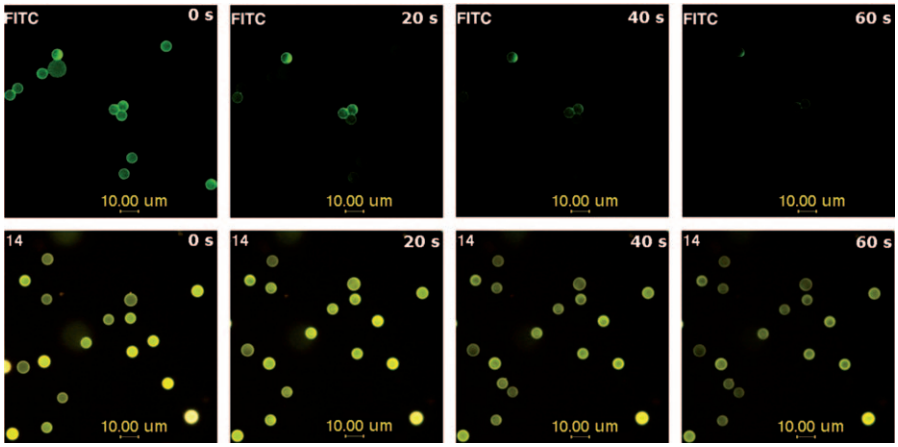


Figure 4. Fluorescence microscopy imaging of FITC and dye **14** conjugated with amino-modified polystyrene microspheres under continuous light irradiation.

Conclusion

We have reported the rational design and synthesis of novel series of thiophene-based fluorescent push–pull dyes characterized by absorption maxima in the range 359–460 nm and photoluminescence maxima in the range 493–650 nm with large Stokes shifts (4300–7500 cm^{-1}), which suggests the possibility of using these labels in bioimaging applications. The modification of π-conjugating units that link the electron-donating and -accepting groups of chromophores is a tool for the development of fluorescent dyes with longer emission wavelengths and a large Stokes shift, which are required for fluorophore candidates for biological applications. The photosensitizing properties of compound **15**, which reacts with singlet oxygen to give sulfine, suggests the possibility of using push–pull terthiophene derivatives in photodynamic therapy.

Experimental Section

Synthesis: The synthesis of all compounds **1**–**15**, their characterizations, and the materials for their preparation are described in detail in the Supporting Information.

Computational methods: All calculations were carried out at the B3LYP/6-31G* theory level using the Gaussian 98 series of programs.[30] Geometries were fully optimized by standard gradient techniques, and the final structures were checked by frequency analysis. An optimization with the full NHS ester group instead of an aldehyde was performed on the d model (the more twisted) to evaluate the effect of the truncation on the core geometry and the inter-ring torsion and the inter-ring distance remained unchanged with respect to the d model.

UV transitions were calculated by 6×6 singly-excited CI ZINDO/S calculations on DFT-optimized geometries by utilizing HyperChem implementation.[31]

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