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Dual emission of *meso*-phenyleneethynylene-BODIPY oligomers. Synthesis, photophysics and theoretical optoelectronic study

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Abstract: Two series of 2,5-di(butoxy)phenyleneethynylenes: one halogenated (n=2,3,4PEC4-X) and the other BODIPY (By) terminated (n=3,4,5PEC4-By), were synthesized monodirectionally by the step-bystep approach and the molecular structure was corroborated by NMR (1H, 13C-DEPTQ-135, COSY, HSQC, HMBC, 11B, 19F) and MALDI-TOF mass spectrometry. The multiplicity and J-coupling constants of ¹H, ¹¹B ¹⁹F/¹¹B NMR signals revealed, in the **nPEC4-By** series, that the phenyl in meso position of the BODIPY becomes electronically part of the conjugation of the phenyleneethynylene chain, while By is electronically isolated. The photophysical, electrochemical and theoretical studies confirm this finding as the properties of nPEC4-By are comparable to those of the nPEC4-X oligomers and By, indicating negligible electron communication between BODIPy and the nPEC4 moieties. Yet, Energy Transfer (ET) from nPEC4 to By was rationalized by spectroscopy and theoretical calculations. Its yield decreases with the nPEC4 conjugation length according to the increase in distance between the two chromophores, resulting in dual emission for the longest oligomer where ET is quenched.

Introduction

BODIPY is the acronym for 4,4-difluoro-4-bora-3a,4a-diaza-sindacene, a π -conjugated complex that since 1968, when its synthesis was first reported,^[1] reached an increasing impact in chemistry and materials science. As an example, we found at the time of writing the article, 12466 references containing the concept "BODIPY" by SciFinder. Indeed, this fused aromatic molecule presents several peculiar properties that made it a building block of a vast catalogue of molecules designated nowadays as "BODIPYs".^[2] First, this complex presents very sharp absorption and emission peaks, with mirror-like excitonic features, large extinction coefficients and (often) high quantum yields. The optical properties can be modulated according to the chemical modification of the BODIPY core; proper substituents can be introduced in the *meso*, α and/or β positions of the pyrrole rings, or on the B atom. The effect on the absorption and emission maxima is usually more important when the chemical modification is realized in the pyrroles. In contrast, a substituent such as a phenyl in the meso position has weak effects in the conjugation because it lies orthogonally to the plane of the BODIPY framework. Nevertheless, this substitution is particularly interesting for tuning the fluorescence quantum yield by favoring energy vs electron transfer. Photoinduced electron transfer (and consequently fluorescence quenching) can be promoted in BODIPYs substituted in the meso position with other not, or less, fluorescent aryls. As such, BODIPY may behave as either electron donor or acceptor depending on the relative oxidation potential of the substituent and the solvent polarity.^[3] Conversely, energy transfer can occur through space via Förster mechanism (FRET) or though bond (TBET).^[4] FRET depends on the spectral overlap between the donor (D) emission and acceptor (A) absorption, the donor-acceptor relative distance and the dipoles orientation. On the contrary, TBET does not require spectral overlap and commonly occurs when a conjugated twisted spacer is used to link the D and A groups. Based on that, the chemical design of BODIPYs has been driven by the final application covering different areas such as molecular probes for cellular imaging,^[5] sensors,^[6] lasers,^[7] LEDs,^[8] near IR absorbers, ^[9,10] solar cells and transistors.[11] For optoelectronics, particularly interesting derivatives have been reported in the last ten years based on the chemical substitutions on the BODIPY with π -conjugated macromolecules.^[12] In this respect, phenyleneethynylenes (PE) are π -conjugated rigid macromolecules that combine high photochemical and thermal stability with usually strong fluorescence, typically in the blue-green region. Because of their stiff cylindrical nature, short π -PE systems have been extensively used as conjugated bridges in several energy transfer systems (also known as energy cassettes) based on BODIPYs and other chromophores, for instance pyrene^[13] or metal porphyrines,^[14] carboranes,^[15], fluorene,^[16-18] among others. The literature on energy cassettes where PE oligomers were directly substituted to BODIPY is, however, quite limited. Some interesting examples.

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Chart 1. Representative phenyleneethynylene (PE) macromolecules bearing BODIPY(s) chromophores, reported in literature as energy transfer cassettes.

are shown in Chart 1. For instance, Yin [19] reported very efficient energy transfer in oligomers end capped with BODIPY of general formula 1, where nPE oligomers with increasing PE moieties (n = 3,5,7) were coupled to one of the α positions of the BODIPY, while the other α position of BODIPYs was functionalized with di-(2pinacolyl) amine. The substitution in this position was intended to give a coplanarity between the two chromophores allowing their electronic communication, in the ground state. Under this assumption, the theoretical modelling indicated that the BODIPY excited state associated with the lower energy absorption peak slightly extended over the first phenyleneethynylene moiety. Consequently, the relative intensity of the BODIPY and nPE absorption bands decreased with n. ET efficiency should decrease with n, but experimentally it was almost constant and larger than 98 %. This behavior was explained on the basis of conformational disorder, which is more important for longer oligomers allowing long-range energy transfer. Y. Cakmak and E.U. Akkaya synthesized the series of phenylethynyl-BODIPy oligomers 2 where BODIPy is functionalized in β position. Remarkable optical properties were found with large red shifts in both absorption and emission spectra. The wide half height band width (HHBW) for the absorption maximum was ascribed to excitonic interactions between the chromophores ^[20] The rigidity driven by the PE unit resulted in a larger Stoke's shift (27-42 nm), with respect to "classical" BODIPys. A similar behavior was also found for the oligobutadyinylene-BODIPy oligomers 3, where BODIPy is again functionalized in β position, with the even more rigid butadyine unit. Interestingly, further derivatization of the dimer gives a water soluble oligomer that can convert from a twisted to a planar conformation, with fluorescence shift from 624 nm to 593 nm, depending on the viscosity of the medium.[21] Indeed the pyrrol substitution of BODIPy covers most of the related literature. The functionalization of PE macromolecules on the boron atom of BODIPY was however also reported for the first time by Ullrich [22] in order to increase the thermal stability and the Stokes' shift of BODIPYs. Following this finding, Nagai [23] synthesized BODIPYs substituted with phenyleneethynylene polymers on the B atom, such as those reported in Chart 1 (4). These derivatives still present the typical emission of the BODIPY fluorophore upon excitation of either, the BODIPY or the PE unit, indicating energy transfer. Moreover, the close neighborhood of the PE branches induces peculiar supramolecular architectures through πinteractions in particles and fibers from the solutions. Mesosubstituents of PEs type can be successfully achieved by Sonogashira-Heck cross-coupling, e.g. from the 8-iodophenyl BODIPY and the corresponding ethynyl terminated PE molecule. By this synthetic strategy, Bodzemir ^[24] obtained the energy transfer cassettes shown in Chart 1, with linear 5, Y 6 and X 7 shapes. In all of the symmetric molecules, labelled as (a) structures, even in the most functionalized molecule, the BODIPY units behave as individual chromophores. In contrast, the introduction of one single stiryl in BODIPY, by the Knovenagel condensation on the methyl pyrrole with p-metoxybenzaldehyde in the (b) structures, converts the molecules in energy transfer

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cassettes, changing dramatically the photophysical properties. Bodzemir defined the energy transfer as FRET; even if he pointed out that TBET could not be excluded as the 1,7-methyl substitution of the BODIPy might drive a near orthogonal arrangement of the BODIPy and the *meso*-phenyl substituent. Conversely, Lindsey reported through-bond energy transfer for porphyrin-BODIPy dyes with phenyleethynylene linkers. In particular, he defined the molecule **8**, Chart 1, as a "linear molecular photonic wire" as the energy is efficiently transferred from the donor BODIPy at one hand ("input") to the free porphyrin at the other hand ("output"), passing through the array formed by three Zn porphyrines linked with diarylethyne segments.^[25]

Based on this background and within our general interest in investigating novel PE based macromolecules for optoelectronic applications, in this work, we report on the synthesis of a series of phenyleneethynylene (PE) oligomers with 2, 3 and 4 moieties, bearing bis-butoxy as side chains, and bromine, iodine (n=2,3,4PEC4-X) or BODIPY (n=3,4,5PEC4-By) as end capping groups, Chart 2.



Chart 2. Molecular structure of the BODIPY (**By**), bromine or iodine phenyleneethynylene oligomers ($n_{=2,3,4}$ **PEC4-X**) and BODIPY phenyleneethynylene ($n_{=3,4,5}$ **PEC4-By**) terminated oligomers synthetized and studied in this work; **By** was used as reference.

In this family, the phenyleneethynylene oligomers are the donor unit as in Bodzemir systems but they are not directly linked to the BODIPy acceptor. A meso-phenyl is used as a conjugated spacer between the growing D segment and BODIPy. Moreover, they bear only one BODIPy at one end and the butoxy of the precursors is kept as the other termini group in order to preserve the solubility. We found, according to the peaks multiplicity of the NMR ¹H, ¹¹B, ¹⁹F signals and the corresponding *J*-coupling constants, the photophysical and electrochemical properties, that BODIPY (By) is electronically isolated, and unperturbed by the nPE conjugation of the oligomers coupled to the phenyl in the meso position, which in contrast becomes part of the nPE conjugation; this was also corroborated by theoretical calculations (vide infra). The orthogonality between both chromophores gives rise to energy transfer from n=3,4,5PEC4 to By as was rationalized by using photophysical and theoretical calculations and its yield decreases along with the length of the nPEC4 oligomer, because of the increasing distance between the two chromophores.

Results and Discussion

Syntheses, Nuclear Magnetic Resonance and MALDI-TOF characterization

The synthesis of the oligomers is carried out by applying the monodirectional divergent-convergent approach. The strategy consists in obtaining four bifunctional monomers: **4**, **11**, **14** and **19**, scheme 1. Their selective cross-coupling through the Sonogashira reaction by the step-by-step approach gives then the oligomers.

The synthesis of the first monomer is achieved in 3 steps starting by the Williamson alkylation of the commercial 4-bromophenol 1 with 1-bromo-butane to obtain 2 in 93 % yield. Then, 2 is Pd/Cu cross-coupled with TMSA in triethylamine to obtain 3 in 69 % vields, which later undergoes desilvlation with TBAF to give 4 in 98 % yields. For the preparation of the second 11 and third 14 monomers, a larger pathway is required. The 1-bromo-2,5di(alcoxy)-benzene 5 is divided in two portions. One portion is subjected to the +NO2 electrophilic substitution formed with concentrated nitric acid in presence of concentrated sulfuric acid; 6 is obtained in 76 % yields. It is worth mentioning that high yield is obtained when 5 is previously dissolved in CH2Cl2 and portionwise added to the mixed acids, instead of adding 5 in powder form. Then, 6 undergoes reduction of the nitro group with Sn/HCI to form the aniline 7. In this respect, and in order to get good yield of 7: 1) 6 must be previously dissolved in THF before adding the Sn and the HCl, 2) the HCl must be added at a rate that allows that the internal temperature does not overpass 5 °C, otherwise the bromine atom is cleaved; 7 is obtained in 64 % yield.

The amine of **7** is used to form an intermediary diazonium salt, which is obtained in quantitative yields (90 %) by a modification of the Schiemann reaction.^[26] Diazonium cation **8** is stable and can be isolated by suction filtration. After its dissolution in a mixture of cold DMF and diethylamine, the triazene **9** is obtained in 68 % yield. Then, TMSA is Pd/Cu cross-coupled to **9** in triethylamine. The acetylene protected monomer **10** is obtained in 86 % yield, which, after its desilylation with TBAF, led to the bi-functional monomer **11** in 96 % yield. The second portion of **5** is selectively iodinated in the para position due to the ortho-para driving effects of both the butoxy and bromine groups to obtain the 1-bromo-2,5-di(butoxy)-4-iodobenzene **12** as the main product in 80 % yield. Then **12** is Pd/Cul cross-coupled with TMSA under the Sonogashira conditions to obtain **13**, from which the acetylene terminated monomer **14** is obtained after desilylation.

The BODIPY **19** is synthetized in 3 steps following the procedure reported by Wang.^[27] Briefly, 4-bromo-benzoylchloride **15** is reacted with 2,4-dimethyl 1H-pyrrole **16** overnight and at room temperature. Triethylamine and BF₃•Et₂O are then added in order to coordinate the boron atom, with relatively low yield of 33 %; **17**, however, can be easily isolated because of its fluorescence that can be followed through the silica chromatographic column with respect to the side products of the reaction. Then, **17** is Pd/Cul cross-coupled with TMSA under the Sonogashira conditions to obtain **18**, from which the acetylene terminated monomer **19** is obtained after desilylation.

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Scheme 1. Reagents and conditions: (a) Br-C₄H₉, NaOH, DMF, 120 °C, 16 h; (b) [(C₈H₅)₃P]₂PdCl₂, Cul, TMSA, Et₈N, 60 °C, 17 h; (c) TBAF, THF, r.t., 1.0 h; (d) H₂SO₄, HNO₃, CH₂Cl₂, 5 °C to r.t., 25 min.; (e) Sn, HCl, THF, 5 °C to r.t., 95 min.; (f) BF₃·Et₂O, t-BuONO, THF, -15 °C, 2 h; (g) Et₂NH, K₂CO₃, DMF, -10 °C, 2 h; (h) TBAF, THF, r.t., 0.5 h; (i) KIO₃, I₂, ACOH, H₂SO₄, H₂O, (92:7:1 vol.), 120 °C, 24h; (j) BF₃·Et₂O, CH₂Cl₂, Et₃N, r.t., overnight.

The monodirectional synthesis of the oligomer series is depicted in scheme 2. The oligomerization begins with the Pd/Cu crosscoupling of **4** with **12** by applying the Godt's protocol,^[28] where aryliodides can be coupled to ethynyls at 5 °C to r.t., while arylbromides need temperature activation of 60-80 °C to perform the cross-coupling reaction. Compound **2PEC4-Br 20** is obtained in 78% yield. One portion of **20** is used for the cross-coupling with BODIPY **19** to obtain the **3PEC4-By 21** oligomer. The other part is subjected to another Pd cross-coupling reaction with the triazene-ethynyl terminated bifunctional monomer **11**. It is worth mentioning that the cross-coupling reaction by using the bromoethynyl **14** monomer is fruitless because **14** tends to selfpolymerize. The triazene terminated trimer **22** is obtained in 50 % yield. Then, triazene is converted into the iodine group with iodomethane in a sealed capsule under vacuum. For this reaction, we found that the yield to obtain **3PEC4-I 23** depends on the precise temperature control at 120 ± 5 °C and on the vigorous stirring of the reaction medium. Then, **23** is divided into two portions; one undergoes Pd/Cu cross-coupling with BODIPY **19** to generate the **4PEC4-By 24** oligomer, while the other part of 23 is subjected to Pd/Cu cross-coupling with **14** under the Godt's procedure to obtain the **4PEC4-Br** oligomer **25** in 63 % yield. The subsequent Pd/Cu cross-coupling of **25** with BODIPY **19** affords the **5PEC4-By 26** oligomer in 44 % yield. As can be seen, following these repetitive reactions cycles, oligomers can be grown up until they reach the limit of their solubility.



Scheme 2. Reagents and conditions: (k) $[(C_6H_5)_3P]_2PdCl_2$, Cul, TMSA, Et_3N, THF, 0 °C to r.t., 48 h; (l) $[(C_6H_5)_3P]_2PdCl_2$, Cul, TMSA, Et_3N, 60 °C, 16 h; (m) CH_3I, 120 °C, vacuum, 15 h.

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The chemical structure of all of the oligomers was confirmed by NMR (¹H, ¹³C-DEPTQ-135, COSY, HSQC, HMBC ¹¹B and ¹⁹F) (ESI). Figure 1a shows the ¹H-NMR spectra of **3PEC4-By** as representative of the series. All of the BODIPY terminated oligomers practically present the same resonant signals: i) differing among them by the number of singlets (s) of the neighbour protons to the alcoxy-phenyls, (16), Figure 1, i.e. 2s for 3PEC4-By, 4s for 4PEC4-By and starting to be additive 5s for 5PEC4-By, ii) the pyrrol protons (2) that appear at 6.015 ppm, do not change with respect to the meso-4-ethynylphenyl-BODIPY 19 δ = 6.007 pm, iii) pyrrol-methyls (6) and (7) in the oligomers resonant at 2.58 and 1.46 ppm, while those of the monomer 19 at 2.57 and 1.41 ppm, respectively, iv) the coupling constants of phenyl in meso position of BODIPY series (n=3.4.5 PEC4-Bv) show very similar values independent of the oligomer conjugation extent of $J_{A-B} = 7.8$ Hz, while those of the *meso*-4-phenylethynyl-BODIPY **19** are of $J_{A-B} = 7.9$ Hz. All of these features suggest that mesophenyl becomes part of the phenyleneethynylene conjugation, while the BODIPY is electronically isolated. The ¹³C-DEPTQ-135 spectra of nPEC4-By series reveal that: i) all of the phenyleneethynylene moieties are different as all of the quaternary ethynylene carbons display differences in number and displacement, i.e., 4 signals for C= in 3PEC4-By, 6 C= in 4PEC4-By and 8 C= in 5PEC4-By, Fig. 9-20S, ii) C(6) and C(7) are isochronous carbons, while their 1H (H6 and H7) are chemically different HSQC, Fig. 6S, suggesting that protons are more sensitive than carbons to the special length of the B and F atoms, iii) all of the pyrrol carbons of BODIPY i.e. C(1), C(2), C(3), C(4), C(6) and C(7) are slightly wider than the rest of the carbons due to the electronic effect of the ^{14}N (I = 1, natural abundance 99.6%), ^{11}B (I = 3/2, natural abundance 80.1%) and ^{10}B (I = 3, natural abundance 19.9%) nuclei with spins higher than 1/2 and possessing Electric Quadrupole Moment (Q), see ¹³C DEPTQ-135, Fig. 11S, iv) carbons of BODIPY oligomers present the same displacement than those of e.g., meso-4-bromophenyl-BODIPY 17. Table 1S.

Figure 1c shows the 11B-NMR spectra of the 3PEC4-By, 4PEC4-By, 5PEC4-By oligomers, which display a triplet at 0.79 ppm due to the coupling of the Boron with the two chemically equivalent Fluor atoms at one bond distance, giving a coupling constant of J = 33 Hz. This result suggests that neither the conjugation extension of 2PEC4-, 3PEC4-, 4PEC4- oligomers nor their coupling with the meso-ethyhnylphenyl alter the BODIPY electronic behaviour. A similar trend behaviour was observed in the ¹⁹F spectra of **2PEC4-By**, **3PEC4-By**, **4PEC4-By**. ¹⁹F spectra show two separately resonant signals assigned to the coupling of 19 F with 11 B (I = 3/2) at -146.25 ppm and to the coupling of 19 F with ^{10}B (I = 3) at 138.5 ppm (not shown). However, the most intense and significant signal for our oligomers is that related to ¹⁹F/¹¹B coupling, which displays four peaks with similar intensity due to the 2nl+1 formalism. In this respect, Figure 1d shows that the displacement of the three oligomers is the same, corroborating that the chemical environment of the BODIPY is the same for the series, in other words, the BODIPY electronic density is not altered by the conjugated oligomers substituted in the meso position.

The macromolecular structures were also corroborated by MALDI-TOF mass spectrometry. The molecular ions for all of the series could be clearly observed with DCTB matrix, either with or without using sodium trifluoroacetate as cationizing agent. Fig. 14S shows the complete spectra for **2PEC4-Br 13** and of the isotopic region for **3PEC4-I 23** and **4PEC4-Br 25**. For **2PEC4-Br 13**: m/z calcd. for C₂₆H₃₃O₆BrO₃: 473.45, found [M⁺⁺] 473.58 and [M⁺⁺ + Na] 496.56; for **3PEC4-I 23**: m/z calcd. for C₄₂H₅₃IO₅: 764.79, found, [M⁺⁺] 764.67 and [M⁺⁺ + Na] 787.67; for **4PEC4-Br 25**: m/z calcd. for C₅₈H₇₃BrO₇: 962.12, found, [M⁺⁺] 962.05 and [M⁺⁺ + Na] 985.08. Fig. 15S shows the isotopic region for the **nPEC4-By** oligomers. For **3PEC4-By 21**: m/z calcd. for C₄₇H₅₁BF₂N₂O₃: 740.74, found [M⁺⁺] 741.01 and [M⁺⁺ + Na] 764.01; For **4PEC4-By 24**: m/z calcd. for C₆₃H₇₁BF₂N₂O₅: 985.08, found [M⁺⁺] 985.27 and [M⁺⁺ + Na] 1008.25; **5PEC4-By 26**: m/z calcd. for C₇₉H₉₁BF₂N₂O₇: 1229.41, found [M⁺⁺] 1229.57 (obtained without using cationizing agent).



Figure 1. a) ¹H-NMR spectra in CDCl₃ of **3PEC4-By 21** oligomer (chemical structure is at top left), b) comparative spectra of the aromatic region of the series, the *meso*-ethynylphenyl-BODIPY **19** is included as a term of comparison, c) ¹¹B spectra and d) ¹⁹F spectra of the series, the multiplicity is generated by the coupling of ¹⁹F with ¹¹B (for I = 3/2 spin).

Photophysical properties

Table 1 collects the photophysical properties in dichloromethane of both series. The *meso*-phenyl-BODIPY (**pBy**), chart 2, is included as term of comparison. Figure 2a shows the absorption spectra of the halogen terminated **nPEC4-X** oligomers, which present two peaks related to the π conjugated backbone: one at ~300-320 nm (band I) ascribed to the HOMO-1→LUMO electronic transition and another one at 334, 376 and 392 nm (band II) that is assigned to the HOMO→LUMO electronic transition. Both bands red-shift and their molecular absorption coefficient ε increases along with the number of the PE moieties. Moreover, the relative intensity of the HOMO→LUMO band with respect to the HOMO-1→LUMO one (In/In) increases within the series. All of these trends are in agreement with the increase of the π conjugation, as observed previously for other PEs^[29] and with the theoretical calculations (vide infra).

A similar behavior is observed when the oligomers are coupled to the BODIPY (**nPEC4-By**), Figure 2b. These two bands are in fact maintained, exhibiting the same trend along the series i.e. a bathochromic shift, an increase in the ε , and of the relative intensity I_{II}/I_L It is worth mentioning that both series of oligomers do not show intra-molecular aggregation, since their UV spectra do not change in shape with the concentration, Fig. 20-21S. Additionally, and as a distinctive characteristic with respect to the halogenated series, the absorption spectra of the BODIPY terminated oligomers: i) present a third band (III), which is

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assigned to the S0→S1 electronic transition of the BODIPY core as it is very sharp, with a half-height band width (HHBW) = 21 nm and a wavelength maximum of 503 nm, similar to that of the reference **pBy**.^[30] The S0→S2 transition of BODIPY core that is found for the reference compound as a weak and broad band at 380 nm, is not observed as it is overlapped by the much stronger transition of the conjugated PE segment. ii) the HHBW of the nPEC4-By band II (HHBWII) increases relative to those of the halogenated nPEC4-X series indicating a larger variety of rotamers around the π conjugated plane, iii) the relative intensity of the nPEC4-By band II with respect to the BODIPY peak (band III), (lu/lu), increases from 0.60 to 0.80 and 1.22, when passing from 3PEC4-By, 4PEC4-By to 5PEC4-By, in agreement with the larger number of π segments. In particular, iv) band III does not shift nor becomes broader in the three derivatives, contrary to what is observed in BODIPY molecules functionalized with phenyleneethynylene segments in the pyrrole positions, where the large Stoke's shift and HHBW are ascribed to electronic interactions among the chromophores.^[20,31] All of these features suggest that BODIPY chromophore is not electronically interacting with the π -conjugated backbone. The maxima wavelength of band II, however, are slightly red shifted, i.e. 46, 12 and 11 nm when passing from nPEC4-X to the nPEC4-By oligomers indicating that the meso-phenyl of the BODIPY is involved in the electronic delocalization of the PE backbone at the ground state, as found by NMR.

The fluorescence spectra, Figure 2c, of the halogenated oligomers exhibit an asymmetric peak with well-structured excitonic type features, which become clearer along as the conjugated chain

6.49

2.00, 2.32, 3.88

2.19, 3.05, 3.81

4.30, 7.39, 6.00

Table 1. Photophysical properties of the halogen and BODIPY terminated oligomers in CH₂Cl₂

increases, suggesting that the largest oligomers, **3PEC4-I** and **4PEC4-Br**, have a more rigid ordered structure than **2PEC4-Br**. The maximum emission wavelength increases with the major number of PE units, in accordance with the larger electron delocalization as observed in the UV-Vis spectra. In general, these features are commonly observed in many other alcoxy PEs that we and others have previously studied.^[29,32] The halogen termini group is expected to promote intersystem crossing because of the heavy atom effect indicated by a lowering of the fluorescence quantum yield ϕ as previously reported.^[29] However, only **2PEC4-Br** has a very weak fluorescence, which actually could not be quantified by the integrating sphere. In contrast, **3PEC4-I** and **4PEC4-Br** present a very high ϕ value. This could be explained considering that for the larger conjugated systems, the halogen is far from the π segment.

In what concerns to the BODIPY terminated oligomers, the fluorescence properties have been measured upon excitation of the BODIPY (band III) and on the PE (band II) absorption. When the excitation is on the BODIPY, for instance for **4PEC4-By** at 493 nm, 10 nm below the maximum absorption peak, the fluorescence spectra present the typical emission band of this chromophore; similar to that of the reference **pBy** with a maximum at around 515 nm. Upon excitation of the PE chromophore at 398 nm, 10 nm below 408 nm, Figure 2d, the emission spectra present additional bands in the range 400-500 nm. Similar observations were found by Yin^[24] and ascribed to energy transfer from the PE to the BODIPY complex, in particular for BODIPYs substituted with phenyleneethynylene oligomers in the pyrrole positions **1**, Chart 1.

52.8/3.10

17.4/1.27

20.3/0.87

15.0/0.91

11.0/1.19

20.0/0.93

31.3/0.99

-

0.09

0.21

0.32

Oligomer	λ _{abs} (nm)	ε (10⁴ M¹cm⁻¹)	HHBW _{II} (nm)	lu/h	lu/lui	λ _{em} (nm)	Δv (cm ⁻¹)	φ _{PE} /τ ^[a] (%)/(ns)	φ _{By} /τ ^[b] (%)/(ns)	k _{radPE} (ns ⁻¹)
2PEC4-Br	298, 335	2.73, 2.39	40	0.87	-	366	2740	-	-	-
3PEC4-I	312, 382	2.67,4.38	57	1.61	-	409	1728	71.8/1.20	-	0.60
4PEC4-Br	318, 397	2.99, 5.92	67	1.96	-	434	2147	94.9/0.99	-	0.96

1.16

1.39

1.72

58

78

81

0.60

0.80

1.22

510

515

515

440, 515

273

463

463

463

λ_{exc}=370 [a] 455 nm [b]

pBy

3PEC4-By

4PEC4-By

5PEC4-By

503

319, 371, 503

319, 394, 503

321, 408, 503

k_{radBy}

(ns-1)

0.17

0.14

0.23

0.16

ФЕТ

(%)

99.6

98.9

47.6

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Figure 2. Normalized (at band II) UV-Vis spectra of: a) halogenated terminated oligomers (nPE-X), b) BODIPY terminated oligomers (nPEC4-By) in CH_2Cl_2 and their corresponding normalized (at maxima emissions) fluorescence for c) nPEC4-X series and d) nPEC4-By in CH_2Cl_2 .

Indeed, the excitation spectrum corresponding to the peak at 515 nm is practically identical to the absorption one. In contrast, that related to the emission at around 440 nm matches only with the PE absorption bands, Figure 3, for 5PEC4-By as an example of the series; see also Fig. 18S. The trend of the fluorescence quantum yield and correspondingly of the radiative constant krad against n and with the excitation wavelength is also in agreement with energy transfer. Considering the chemical structure of nPEC4-By where. according the photophysical, to electrochemical and theoretical (see further) results, the mesophenyl becomes part of the donor PE conjugation and BODIPy is orthogonal to the π conjugated plane, even in the longest oligomer, we can infer that the main mechanism of energy transfer is likely TBET. Nevertheless, as the main different feature between FRET and TBET is the energy transfer rate, which is much faster for TBET, ultrafast spectroscopy will be carried out in the continuation of the work to corroborate this issue. An estimation of the energy transfer efficiency ϕ_{ET} is usually performed on the basis of the Förster theory, which can be obtained by steady state or dynamic fluorescence ($\phi_{\text{ET}=}$ 1-I/I₀= 1- τ/τ_0). Since, the absorption results indicate that the conjugation involves also the meso-phenyl of the BODIPY, therefore these equations cannot be used in our case. Nevertheless, a rough estimation of the energy transfer efficiency can be obtained by integrating the area under the spectra corresponding to the PE emission (400-500 nm) with respect to the total area. Under this approximation, the values of ϕ_{ET} are reported in Table 1 showing that the energy transfer is very efficient for 3PEC4-By and 4PEC4-By and less for 5PEC4-By, which consequently presents a larger fluorescence quantum yield

when excited on the PE absorption; actually, a dual emission was found for this oligomer. In conclusion, ET yield decreases with the nPE conjugation length (see theoretical calculations). Interestingly, dual emission was also found in energy transfer systems, where the acceptor *meso*-phenyl BODIPY was introduced at the middle of a donor fluorene oligomer with 3, 5 or 7 units. Indeed, similarly to our study, the authors found that energy transfer was quenched only in the longest oligomer, which showed dual emission from both oligofluorene and BODIPY units.^[16] This strategy was then extended to polymers and dual emission was observed even in solid state films, which is actually our next work in view of an optoelectronic application of the present dyes.^[17,18]

As an additional characterization of the emission properties of the **nPEC4-By** dyes, the CIE1931 coordinates (X,Y) were calculated by the fluorimeter software. The (X,Y) of the oligomers, those of the dominant color (Xd,Yd) and the color purity values are collected in Table 2S (ESI). Figure 4 shows the corresponding CIE1931 color diagram; while **3PEC4-By** and **4PEC4-By** emission is close to the green periphery with similar coordinates and color purity, **5PEC4-By** gets close to the white color (X_c, Y_c=0.33, 0.33), because of the dual emission. This property could be important for future applications in white oLEDs.



Figure 3. Excitation spectra at 515 nm (black squares) and 454 nm (red circles) for **5PEC4-By** in CH_2Cl_2 and its UV spectrum (blue triangles); spectra were normalized with respect to the PE band (II).



Figure 4. CIE 1931 colour diagram for nPEC4-By oligomers in CH₂Cl₂: 3PEC4-By (square), 4PEC4-By (circle) and 5PEC4-By (triangle).

FULL PAPER Electrochemical properties

We used cyclic voltammetry to evaluate the electronic effect of the phenyleneethynylene oligomers coupled to the meso-phenyl of the BODIPY with respect to pristine **pBy**. The electrochemical data are summarized in Table 2. For comparison, Figure 5a shows the voltammograms of the pBy, 3PEC4-I and the 3PEC4-By as representative of the series. According to the molecular electrostatic potential map (EPM) of the iodine-terminated oligomer, Figure 5b, which is almost the same for this series of oligomers, Fig. 22S, two high electronegative sites susceptible to redox process can be identified and are visualized in red (abundance in electrons): on the alcoxy and ethynylene groups. As a term of visualization, the acetvlene terminated trimer 3PEC4-En, Fig. 22S, is also included, which clearly shows that the acetylene is a highly susceptible group to the redox process. A slight electronegative density site, colored in yellow, could be identified in the central part of the phenyls and close to the halogens, while the lowest electron density, colored in blue, is located around the hydrogens. In what concerns to pBy, interestingly, the meso-phenyl is completely colored in blue, while the pyrrol rings are green-yellow colored, being the highest electronegative sites in the N-B-F coordination center. This could explain why meso-phenyls (that is out of the plane) bearing different functional groups, such as meso-4-bromophenyl, present almost the same potential redox bands between them, Fig. 23S, meaning that phenyls do not participate in the redox process. The n=2,3,4PEC4-By oligomers present the following peculiar behavior: i) meso-phenyl becomes electronically part of the PE-oligomers. ii) yellow-green colors are found all along the nPE conjugated meaning that electrons density skeleton. becomes homogeneously distributed and not only located in the ethynylene segments, and iii) the highest electronegative sites are located in the alcoxy groups and in the pyrrol-N-B-F coordination center, supporting what we have found by NMR and photophysical characterization, that BODIPY has no electronic communication with the PE chains, likely because conjugation is interrupted due to their reciprocal orthogonality.

The voltammogram of pBy shows the following features already reported in the literature: two electron reversible redox potentials. which are very well defined at scan rates higher to 100 mV/s, Fig. 22S, even observed at 1000 mV/s,^[33] while at low scan rates, e.g. 20 mV/s, redox processes are almost perceptible, [34] Fig. 24Sa. In our case, the oxidation at the maxima potential, E_{ox} , is= +1.35 eV and the reduction, *E*_{red} = -1.34 eV, Table 2. In contrast, the halogen terminated oligomers nPEC4-X, rather show a medium electron transfer rate, because potentials are well defined at 50 and less at 20 mV/s, but not at 100 mV/s; where undefined and broad bands are seen in the voltammograms, Fig. 24Sb. We observed, that: i) halogen terminated oligomers exhibited up to three anodic oxidation peaks with high current intensities and two cathodic reduction peaks with low current intensities, being this disproportionality related with the high electron donor character of the oligomers, ii) either a decrease in the oxidation or the reduction potential is observed at less negative potentials, related to the more extended π -electron delocalization, such as was also observed by UV-Vis spectroscopy. Interestingly, the BODIPY terminated oligomers, nPEC4-By, display a slight anodic and cathodic shift with respect to nPEC4 precursors, but with a decrease trend between them of the redox potentials as a function of the conjugation extension. It is well known that the larger the PE (symmetrical) oligomers are, more difficult becomes to oxidize or

reduce them.^[27] In general, all of these oligomers showed the reversible reduction peak of **pBy** with a slight shift to cathodic values, Figure 5 green signalization, suggesting that no significant interaction takes place between both electroactive chromophores in the ground state.



Figure 5. Comparative cyclic voltammograms of *meso*-phenyl-BODIPY (**pBy**), 3PEC4-By and 3PEC4-I oligomers analyzed in CH₂Cl₂ (3 mmol), using 0.1M of Bu₄NPF₆ as electrolyte at scan rate of 50 mV/s (**pBy** at 100 mV/s), (V vs Ag/AgCl) and GC as working electrode, b) electrostatic potential map of **pBy**, 3PEC4-By and 3PEC4-I oligomers obtained from the optimized molecular geometry by B3LYP functional.

Table 2. Electrochemical properties of the halogen and BODIPY terminated oligomers in CH₂Cl₂ containing Bu₄NPF₆ (0.1M) as the supporting electrolyte Vs Ag/AgCl and at 50 mV/s.

Oligomer	E ^{max} (V)	E ^{max} (V)	HOMO (eV)	LUMO (eV)	Eg (eV)
2PEC4-Br	-0.92	+1.40	-6.20	-3.88	2.32
3PEC4-I	-0.83	+1.25	-6.05	-3.97	2.08
4PEC4-Br	-0.77	+1.25	-6.05	-4.03	2.02
рВу	-1.34	+1.35	-6.15	-3.46	2.69
3PEC4-By	-1.22	+1.29	-6.09	-3.58	2.51
4PEC4-By	-1.20	+1.28	-6.08	-3.60	2.48
5PEC4-By	-1.09	+1.20	-6.00	-3.71	2.29

Theoretical calculations

All of the **nPEC4-X** and **nPEC4-By** oligomers were analyzed by DFT and DLPNO-STEOM-CCSD methods. It is known that the standard TD-DFT protocol does not predict precisely the BODIPY electronic properties.^[36] However, recently, Berraud-Pache et al. developed the DLPNO-STEOM-CCSD approach for BODIPYs,^[37] By our side, we found that this latter formalism gave good correlation between the calculated and experimental electronic properties for **nPEC4-By**. Thus, for the first time for our knowledge, this new procedure was applied to **nPEC4-X** series, with aim to maintain the study continuity. The geometry of each oligomer was first optimized in vacuum using B3LYP functional for **nPEC4-X**, while for **nPEC4-By** series, after having evaluated different functionals, the range-separated hybrid CAM-B3LYP was chosen due to the lower CC energy obtained in comparison to B3LYP. Previously, its efficiency was proven by Petrushenko for different

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BODIPY containing systems.^[38] Then, ESD module was applied to obtain the geometries of the first excited state using the vertical gradient (VG) approximation, to finally give, by following the DLPNO-STEOM-CCSD protocol, the excitation energies in vacuum and in CH₂Cl₂ for both ground and excited state geometries; corresponding to absorption and emission energies. These values, together with the transitional dipoles, were used to get the absorption and emission spectra including the solvent effect via the Conductor-like polarizable continuum model. In this respect, and in order to predict properties with a high accuracy and reduced computational costs, the Herzberg-Teller effect was estimated just for the smallest compounds of the series.

The **nPEC4-X** oligomers. Fig. 6 and Fig. 25S, show π -type molecular orbital features, being the HOMO and LUMO delocalized all along the conjugated backbone. In particular, the HOMO orbitals are formed of π -bonding lobes, mainly centered on the conjugated backbone including the alcoxy substituents, which are electron donor groups, while the LUMO orbitals are rather of single lobes or antibonding orbitals. In contrast, nPEC4-By oligomers show different frontier molecular orbital (FMO) distribution all along the conjugated structure. The FMO images, Fig. 6 and 26S, show that HOMO-1 and LUMO are localized on the BODIPY core, while HOMO and LUMO+1 on the conjugated backbone. In this respect, the optimized structure of **pBv** as a model compound shows a dihedral angle of 90° between the meso-phenyl and the BODIPY complex that according to Chen.^[39] is due to the steric hindrance generated by the methyl groups substituted in the 1,7 positions. The same tendency is observed for the nPEC4-By oligomers, supporting what was found by NMR that the π conjugation extends from the *meso*-phenyl to the PE conjugated chain, leaving the BODIPY electronically isolated. In whole, these results corroborate the findings of the photophysics and electrochemistry studies; the BODIPY and PE chromophores, despite being acceptor and donor units, respectively, maintain their individual electronic characteristics, i.e. there is no electronic communication between them because of their mutual orthogonality.[40]



Figure 6. Frontier molecular orbitals of representative oligomers of the series.

To further understand the photophysical properties of **nPEC4-X** oligomers, we obtained simulated absorption (S0 \rightarrow S1) and emission (S1 \rightarrow S0) spectra. Previously, we used a combined method^[41] to treat the problem of a big discrepancy between

experimental and computed data for such systems. This time, we used DLPNO-STEOM-CCSD to calculate excitation properties in CH₂Cl₂ and data are summarized in Table 3. The first singlet excitation is dominated by the HOMO \rightarrow LUMO electronic transition, in agreement with the higher percentage contribution. The HOMO \rightarrow LUMO+1 transition is also involved, but with lower contribution. Comparing Table 3 with Table 1, one can see that the theoretical photophysical properties match well those of the experimental data, not only for absorbance but also for emission, which usually is a challenge for similar PE systems. The computed electronic spectra, Fig. 7 and Fig. 27S well resemble those of the experimental spectra of Figures 2a and c. Indeed emission simulated spectra present excitonic like features, which become more notorious as the length of the conjugated backbone increases, as found experimentally.



Figure 7. Computed normalized absorption of: a) **nPEC4-X** and b) n = 2 (**4PEC4-By**, n = 3 (**5PEC4-By**) and **pBy** oligomers obtained by the DLPNO-STEOM-CCSD protocol developed by Berraud-Pache^[37] for BODIPY compounds.

To get further insight of the photophysical processes between donor-PE and acceptor-By in the nPEC4-By series, we also obtained their excitation properties in vacuum following the DLPNO-STEOM-CCSD protocol, Table 3, Fig. 7 and Fig. 28S. It can be clearly seen that HOMO-LUMO gap decreases within the series, just because of the lowering of the HOMO orbital, which is related to the PE conjugated segment; in fact, the LUMO, attributed to BODIPY segment, keeps constant at -1.52 eV, practically as pBy, as was observed in the electrochemistry. pBy presents two main electronic transitions; one with excitation energy E_{exc} of 3.80 eV, which corresponds to the S0 \rightarrow S2 excitation, where HOMO-1 and LUMO orbitals are involved, and another one, Eexc= 2.40 eV that is the S0-S1 electronic transition involving the HOMO and LUMO orbitals. The corresponding wavelengths at 326 and 517 nm match very well the experimental values. For the nPEC4-By oligomers, these two excitations are maintained where the lower energy one Eexc~2.40 eV is still attributed to the (S0-S1) of BODIPY, while the higher energy Eexc=3.48-3.32 eV is due to the PE moiety. It can be seen that the latter redshifts with the PE length as observed in the experimental photophysical studies. Conversely, there is not a trend in the relative intensity ratio of the PE/BODIPY bands, which can be justified considering that the calculation of the intensity with the DLPNO-STEOM-CCSD protocol is not precise. In what concerns the emission spectra, pBy and 2PEC4-By show more red-shifted bands than 3PEC4-By and 4PEC4-By, which can be related to the

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Oligomer	HOMO (eV)	LUMO (eV)	HOMO-LUMO (eV)	E _{exc} (eV)	λ _{abs} (nm)	λ _{em} (nm)	Δv (cm ⁻¹)	Transitions (%)
2PEC4-Br	-5.24	-1.33	3.91	3.78	328	361	2787	HOMO→LUMO (96.43)
3PEC4-I	-4.94	-1.71	3.23	3.32	373	407	2240	HOMO→LUMO (97.31)
4PEC4-Br	-4.79	-2.06	2.73	3.10	400	438	2169	HOMO→LUMO (97.92)
рВу	-6.73	-1.54	5.19	3.80, 2.40	326, 517	539	789	
3PEC4-By	-6.53	-1.52	5.01	3.48, 2.40	356, 517	538	755	
4PEC4-By	-6.29	-1.52	4.77	3.38, 2.41	367, 514	522	298	
5PEC4-By	-6.14	-1.52	4.62	3.32, 2.42	373, 512	524	447	

Table 3. Calculated excitation properties of nPEC4-X in CH₂Cl₂ and nPEC4-By in vacuum of the series of oligomers by using the DLPNO-STEOM-CCSD method.

more distorted excited state geometry obtained via vertical gradient approximation and not completely optimized module by Orca software. The excited states of **nPEC4-By** oligomers were also analyzed as electron difference density (EDD) plots, which clearly show if charge transfer occurs in a D-A system. Fig. 8 reports EDD plots of two excited states for each oligomer. It can be seen that both states have character of local excitation, where the first excited state is completely associated with BODIPY core's excitation, while the second excited state is attributed to the conjugated PE backbone, confirming that there is no charge transfer between PE and BODIPY. Therefore, the fluorescence quenching observed in the experimental photophysical analysis can be associated to energy transfer.



Figure 8. Computed density difference plots between the excited and ground states of the **nPEC4-By** series. Red (blue) regions indicate increase (decrease) of the density upon ab-sorption. The selected contour threshold is 0.0004 au.

Conclusion

Two series of oligomers, 1) bromine or iodine terminated phenyleneethynylenes with 2, 3 and 4 moieties ($n_{2,3,4}$ PEC4-X), and their Sonogashira cross-coupling to a *meso*-4-ethynylphenyl-BODIPY to form 2) $n_{3,4,5}$ PEC4-By oligomers were selectively, step-by-step synthetized. The peak multiplicity, the (¹H, ¹¹B) *J*-coupling constants and the invariant chemical shifts of the carbons signals (C(1), C(2), C(3), C(4), C(6) and C(7)) in the BODIPY structure determined by NMR spectroscopy revealed for the **nPEC4-By** series that the phenyl in *meso* position to the BODIPy (**By**) becomes part of the electronic conjugation of the

phenyleneethynylene oligomers, while By is electronically isolated due its orthogonality. The UV-vis spectroscopy confirmed this increase of nPE conjugation because the wavelength assigned to the HOMO \rightarrow LUMO transition of the **nPEC4-X** oligomers of λ max = 335, 382 397 nm for 2PEC4-Br, 3PEC4-I, 4PEC4-Br, respectively, red shifts for the **nPEC4-By** series, to $\lambda_{max} = 371, 374$, 408 nm for 3PEC4-By, 4PEC4-By, 5PEC4-By, respectively, while the S0 \rightarrow S1 transition of the BODIPY keeps always at λ max = 503 nm. Conversely, the absorption spectra of the nPEC4-By oligomers almost match the sum of the individual component spectra (also in shape) i.e. of nPEC4-X and pBy, confirming that there is no electronic interaction between the two chromophores in the ground state as also found by electrochemistry and corroborated by theoretical calculus. In contrast, in the excited state, Energy Transfer (ET) was found to occur from (n=3,4,5PEC4) to By, and its yield decreases with increasing nPE conjugation, which is in agreement with the increase in the distance between the two chromophores, yielding dual emission for the longest oligomer. The electrochemical and photophysical properties of the BODIPY terminated oligomers suggest their possible application as dye sensitizers in photovoltaic or electroluminescent devices.

Experimental Section

Synthesis

Experimental procedures, chemical and physicochemical characterization of each compound are given in the electronic supplementary section (ESI).

Equipment and methods

One dimensional; ¹H (400 MHz), ¹³C-DEPTQ-135 (100.5 MHz), ¹¹B (128.3 MHz) and ¹⁹F NMR (376.5 MHz) and two dimensional (COSY, HSQC, HMBC) NMR spectra were obtained at room temperature with a 400 MHz Bruker Avance III HD 400N (with a 5 mm multinuclear BB-decoupling probe, direct detection with Z grad). Some ¹H and ¹³C spectra were obtained on a Jeol Eclipse 300 MHz spectrometer. In the cases of ¹¹B and ¹⁹F, the spectra were acquired under regular proton decoupling conditions. Chemical shifts (ppm) are relative to remaining non-deuterated chloroform signal (from CDCl₃) and used as internal reference for ¹H and ¹³C. For ¹¹B NMR spectra, the external reference was BF₃•OEt₂ and CFCl₃ for ¹⁹F NMR spectra. MALDI-TOF mass spectra were obtained on a Bruker Autoflex Speed TOF/TOF operated in reflector mode and using a DCTB matrix in the positive ion mode; sodium trifluoroacetate or NaCl was used as the cationizing agent. The photophysical properties were analysed in an

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acclimatized room (17℃) in spectroscopic dichloromethane. UV-Vis spectra were obtained with a Shimadzu 2401 PC UV/VIS spectrophotometer. The extinction coefficient ϵ was determined from the slope of the absorbance vs. molar concentration of at least four solutions. The excitation and emission spectra were obtained with an Horiba PTI Quantamaster QM-8450-22-c spectrofluorimeter equipped with an integrating sphere for the determination of the guantum yield. All of the spectra were obtained with background correction and with the same slits and bias between the sample and the solvent. Slits were established in order to keep the uncorrected spectra under the linear range of detection (10⁶ counts). The excitation wavelength was 10 nm below the main absorption peak and the absorbance at that wavelength was adjusted to be lower than 0.1. At least four solutions were analysed for each complex and the quantum yield was averaged and reported as ϕ . Stokes' shift (Δv) values were calculated from the absorption and fluorescence maximums in wavenumbers (λ_{emis} - λ_{abs}). CIE 1931 coordinates were found by the fluorimeter software and the CIE colour diagram was constructed with goCIE free software. The colour purity was calculated based on the following equation:

colour purity= $\sqrt{((x-x_c)^2+(y-y_c)^2)}/\sqrt{((x_d-x_c)^2+(y_d-y_c)^2)}$

where (x;y) are the colour coordinates for the material, x_d and y_d are those of the dominant colour, which are obtained from the intersection of the line connecting the (x,y) point with perfect white light (xc, yc) = (0.33, 0.33).

Average fluorescence lifetimes $(\boldsymbol{\tau})$ were obtained by the time correlated single photon counting (TCSPC) technique on an Horiba Jobin Yvon TemPro instrument with a nanoLED laser of a wavelength close to the wavelength used for the emission spectra. Fits were performed on the DAS6 software of the instrument. Radiative (kr) constants were calculated from the equation: kr= ϕ/τ . A 0.01% suspension of Ludox AS40 (Aldrich) in ultrapure water was used for the prompt signal. Calibration of the equipment was realized with a POPOP [4-bis(4-methyl-5-phenyl-2oxazolyl)benzene] methanol solution (optical density 0.1 and lifetime of 0.93 ns).^[42] The electrochemical properties of all of the compounds were investigated via cyclic voltammetry in a Stand cell from Basi, coupled to a Squidstat Plus potentiostat/galvanostat from Admiral Instruments. The system consisted of a conventional three-electrode cell: classy carbon as a working electrode (polished with alumina and diamond powder after each run), Pt wire as the counter electrode, Ag/AgCl as reference electrode (viability of -35±20 mV against the Calomel electrode) and ferrocene/ferrocenium (FOC) as external reference (Eox = 5.1 V, Ered = 3.8 V, formal potential (E°) of 0.436 V); value of -4.8 eV below the vacuum level. Voltammetry measurements were performed at room temperature in dry CH₂Cl₂ containing Bu₄NPF₆ (0.1M) as the supporting electrolyte. Prior to recording the voltammograms, the electrolyte solution was deoxygenated by bubbling nitrogen for at least 15 min. The experiments were carried out under a nitrogen atmosphere at a scanning rate of 50-100 mV/s for a complete cycle between -3.0 and +3.0 V and in separated windows. The molecular orbital energies HOMO and LUMO were calculated from the first oxidation (E_{ox}) and reduction (E_{red}) maximum potentials with the relationship: *E*[HOMO][LUMO]= -exp(*E*(Ox[red] vs. Ag/AgCl)) - 4.80. The electrochemical energy gap was the difference between the HOMO and LUMO values, E_q = HOMO-LUMO.

Theoretical calculations

All of the calculations were performed with the ORCA program package version 4.2.1.^[43] The molecular structures were drawn by using the free software Gabedit version 2.4.8.^[44] In order to reduce the computational costs, alkyl chains were replaced by methyl groups. Geometry optimization was performed following the next procedure: all molecular structures in the ground state were first optimized by HF-3c method.^[45] After that, the geometries of **nPEC4-X** oligomers were further optimized in vacuum using the B3LYP^[38] functional with the def2-SVP^[46] (for C, H and O atoms) and def2-TZVP (for Br and I) basis sets in combination with Grimme's dispersion correction^[47,48] and the RIJCOSX approximation^[49] as well as

with auxiliary basis set.^[50] For the BODIPY- terminated oligomers (**nPEC4-By**), the HF-3c geometries were further optimized with CAM-B3LYP^[51] functional using the def2-SVP basis set. The Hessians were obtained for all of the structures showing no negative frequencies, i.e. all optimized structures are true minima. The DLPNO-STEOM-CCSD method, which previously showed a remarkable precision for **nPEC4-By** oligomers,^[62] was applied to predict photophysical properties of **nPEC4-X** oligomers, using the first six singlet excited states to calculate the excitation energies and transition dipoles on the optimized ground state geometry taking into account the solvent (dichloromethane) effect by using the conductor-like polarizable continuum model (C-PCM). The vertical gradient was applied to the excited state-dynamic (ESD) module, which admits that Hessian of the excited state is equal to the ground state one and extrapolates the excited state geometry from the excited state gradient.

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Meso-phenyl-BODIPY, coupled to phenyleneethynylene (PE) oligomers, is electronically isolated from the π -PE conjugation because of its orthogonality, but displays high energy transfer (ET) efficiencies or dual emission.

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