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Introduction

The electron attracting character of the -C = N- group (A) of quinoline based materials¹ generates a push-pull effect between an electron donor group (D), such as 2,5-di(alkoxy)benzene, through a π -conjugated connector (A- π -D- π -A) that in turn provides efficient intramolecular charge transfer (ICT), which makes these materials suitable for linear, nonlinear optic (NLO) and photovoltaic (PD) devices. Among the different architectures of quinoline based macromolecules, *i.e.*, linear,² asymmetrical,³ polymer like⁴ or dendrimer,⁵ monodisperse oligomers are of special interest as optoelectronic materials. As such, they are models that help to understand the properties of their polydisperse homologous polymers. Despite that, the synthesis of the monodisperse oligomers usually involves numerous steps as well as a tedious purification workup. Their effective conjugation, however, is sometimes achieved with

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Synthesis and optoelectronic properties of phenylenevinylenequinoline macromolecules†

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A series of 3, 5 and 7 quinoline terminated arylenevinylene oligomers was selectively synthesized by applying two repetitive reactions at each cycle of oligomerization: a Wittig and Pd Heck cross-coupling. Oligomers were characterized by ¹H and homo-*J*-resolved, DEPT-135, APT, ¹³C NMR and MALDI-TOF spectrometry. A detailed characterization of the oligomers was performed by UV-Vis, static-dynamic fluorescence and Z-scan spectroscopy. The HOMO and LUMO levels were determined by cyclic voltammetry and compared with the theoretical ones. Effective conjugation is attained for the pentamer, whilst the molecular structure of the heptamer shows a pronounced torsion of the phenylenevinylene segment disrupting the degree of conjugation as revealed by theoretical simulation of the oligomer geometry. Furthermore, the theoretical simulation shows that the HOMO–LUMO frontier orbitals are mainly localized in the phenylenevinylene structure, while in the quinolines the spatial distribution is only located at the C==N– group without any appreciable contribution of the adjacent phenyl group. The pentamer is the most fluorescent oligomer with a quantum yield in solution of $\phi = 0.62-0.68$ depending on the solvent and a fluorescence lifetime of 1.07–1.28 ns, making this oligomer suitable for optoelectronic devices.

> shorter oligomers such as heptamers and pentamers. In quinoline based oligomers for instance, it has been demonstrated that even dimers exhibit efficient ICT. Whilst trimers, polymers or dendrimers may be used as active emitting layers in OLEDs, their main application is as n-type materials for electroluminescence (EL) efficiency enhancement layers in emitting polymers such as MEH-PPV.²⁻⁵ Because of our interest in obtaining new materials with NLO and efficient ICT properties, we designed and synthesized odd numbered quinoline terminated oligomers following the original idea of Wang,² who found excellent EL properties for similar trimers, in particular, for those bearing 2,5-di(methoxy)benzene as a donor and a solubilizing group. In our design, we replaced the 2,5-di(methoxy) group by 2,5-di(dodecanoxy) solubilizing chains and increased the phenylenevinylene segments in order to obtain a pentamer and a heptamer with both efficient ICT and emitting properties. However, we found minor optoelectronic differences between the pentamer and the heptamer marked by a pronounced torsion of the conjugated chain that is dependent on the oligomer's length. In addition to our spectroscopic and voltammetry study, theoretical calculations suggest that quinoline as an electron acceptor (A) must be centered as closest as possible to the electron donor (D) in order to favor an ICT between $D \rightarrow A$ groups; a result that will be taken into account for the design and synthesis of new n-type macromolecules.



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Synthesis

A central oligomer **3** was synthesized in order to grow oligomers in odd number at each cycle, Scheme **1**. By reacting one equivalent of **1** with 2 equivalents of 4-bromo styrene and using the modified catalytic system reported in the literature, which in our case was composed of Na(OAc₂) (1.2 eq.), $^{-}Br^{+}NBu_{4}$ (0.2 eq.), POT (0.04 eq.) and Pd(OAc₂) (0.02 eq.) in DMF–Et₃N (90/10 v/v), we could carry out the reactions at 130 °C with bromoaryls, without promoting the thermal decomposition of the catalyst and with a preferable all *E*-isomer formation; **3** was obtained in 70% yield with a calculated coupling constant of the vinylic protons of J = 16.5 Hz confirming the AB system with an *E* isomerization.⁶

The oligomer synthesis consisted of applying the two repetitive Wittig and Heck sets of reactions; the general pathway is depicted in Scheme 2. The commercially available 2-quinolinecarboxaldehyde 4 is reacted with methyltriphenylphosphonium bromide under Wittig conditions to give the 2-vinyl-quinoline 5 in 75% yields. Then 5 is divided into three portions from which two equivalents of one portion is reacted with one equivalent of 1,4-bis(dodecanoxy)-2,5diiodo-benzene 1 to afford the E-3QPV oligomer in 78% yields. The other two equivalents of the second portion of 5 is reacted with one equivalent of 3 to yield the E,E-5QPV oligomer in 60% yield. The third portion of 5 undergoes a Heck cross-coupling with commercial 4-bromobenzaldehyde 8 to yield an aldehyde terminated 9, which after a Wittig reaction generates the double bonds, 10 was obtained in 88% yield. The E,E,E-7QPPV oligomer is obtained in 47% yield by reacting two equivalents of 10 with one equivalent of 3. It is worth mentioning that E,E,E-7QPPV is soluble either in CHCl₃, toluene or THF and precipitates in polar



Scheme 1 Reagents and conditions: (a) Pd(OAc)₂, ⁻Br⁺NBu₄, CH₃COONa, POT, DMF, 130 °C, 48 h.

solvents such as methanol, acetone and acetonitrile. Moreover, **7QPPV** in its entirely (*E*) configuration is easily isolated from the rest of the unreacted (*Z*) and (*E*,*Z*) mixtures of isomers, due to its solubility only in hot $CHCl_3$ or toluene; this behaviour made it almost impossible to record its ¹³C NMR spectra; its molecular structure was confirmed by MALDI-TOF spectrometry.

The oligomers are symmetrical, so the ¹H NMR spectra could be accurately assigned, however as the molecule became longer, the aromatic region became more complex as the quinoline protons overlapped with those of the phenylenes and vinylenes, while the aliphatic region of all of the oligomers is well resolved showing the $-O-CH_2$ - α , β and γ signals at 4.06, 1.89 and 1.56 ppm. The signals of -CH2- and -CH3 are centred at 1.25 and 0.68 ppm, respectively. Since the spectroscopic and optoelectronic properties of the oligomers depend in large measure on their cis or trans configurations, unambiguous assignment of vinylenes was carried out by recording their ¹H J-resolved spectra (JRES). As an example the JRES spectrum of the E,E-5QPV is presented in Fig. 1. Two-dimensional JRES NMR spectroscopy retains many of the benefits of 1D NMR, but additionally disperses the overlapping of those with high signal density regions into a second dimension, reducing congestion and making easier the assignment of some signal; however couplings to long distances are also present. Notice, for example, that HB and HD protons resonate in a very complex region, but are easily assigned in the 2D spectrum. Due to characteristic equalities in coupling constants of J 16.23 Hz for HA (at 7.42 ppm), HB (at 7.68 ppm) and of J 16.09 Hz for HC (at 7.15 ppm) and HD (at 7.53 ppm), the E,E isomer of 5QPV is so confirmed. In addition, signals of the phenyl protons H9 and H10 are easily recognised with corresponding coupling constants of 8.3 Hz because of the AB system. Furthermore, positive matrix-assisted laser desorption ionization-time of flight mass spectrometry (MALDI-TOF-MS) corroborated the oligomers' molecular structure by showing their expected molecular ion peak:⁶ for 3QPPV: m/z 752.4 (M^{•+}, calcd for C₆₄H₁₀₆O₄: 752.5); for 5QPPV: m/z 956.58 (M^{•+}, calcd for C₁₂₈H₂₁₀O₈: 956.62) and for 7QPPV: *m/z* 1160.72 $(M^{\bullet^+}, \text{ calcd for } C_{192}H_{314}O_{12}: 1160.72).$



Scheme 2 Reagents and conditions: (a) MTPP-Br, t-BuOK, THF, rt, 24 h; (b) Pd(OAc)₂, CH₃COONa, ⁻Br⁺NBu₄, POT, DMF, 130 °C, 72 h.



Optical properties

In order to study the effect of the quinoline on the optoelectronic properties of the **nQPV** oligomers, three other trimers were incorporated in the discussion; 1,4-di(*E*)-styrylbenzene (**DSB**), 1,4-bis-(dodecanoxy)-2,5-di(*E*)styrylbenzene (**3C12DSB**) and 1,4-bis((*E*)-4-bromostyryl)-2,5-bis(dodecyloxy)benzene (**3BrPV**), Chart 1.



Chart 1 Molecular structure of trimers used as comparatives models in the different characterization techniques: (DSB) 1,4-di(*E*)-styrylbenzene, (**3C12DSB**) 1,4-bis(dodecanoxy)-2,5-di(*E*)styrylbenzene and (**3BrPV**) 1,4-bis((*E*)-4-bromostyryl)-2,5-bis(dodecyloxy)benzene.

All of the optical properties of the materials studied in this work are summarized in Tables 1 and 2, while the UV-Vis spectra of the nQPV family and those of model trimers in chloroform are shown in Fig. 2. From this figure, several absorption features depending on the molecular structure can be observed: (i) the electron donor character of the 2,5-bis(dodecanoxy) chains increases the conjugation by a wavelength shift from 337 nm (sh 354 nm) (lit⁷ 354 nm) for the DSB to 388 nm (lit⁸ 388 nm) for the 3C12DSB and (ii) to 391 nm for the additional contribution of the electron donor of the bromine atoms in the trimer 3BrPV, (iii) electronic absorption spectra of the trimers with 2,5-bis(dodecanoxy) chains are characterized by an intense broad band and a higher energy absorption peak at around 235 nm. According to theoretical calculations, the red shifted band can be associated with the electronic transitions from the HOMO to the LUMO, while the higher energy absorption to those between lower lying occupied molecular orbitals (HOMO $\{-1\}$, HOMO $\{-2\}$) to LUMO, (iv) this energy band (235 nm) is red shifted but less intense by both the presence of the quinoline and as a function of the oligomer length.

The three spectra of the **nQPV** present a main peak due to the π - π * electronic transition of the conjugated backbone, between 418 and 433 nm, in the same range of those reported for other OPVs.9 Along with the conjugation, the molar absorption coefficient of the maximum increases while its wavelength red shifts, even if the increase between the 5QPV and the 7QPV is of only three nm, suggesting that the effective conjugation length is already gained with 5 units. This is more evident by the trend in the band gap, which is practically identical between 50PV and 70PV. It is worth noting that no changes in the spectra were observed with concentration or the solvent polarity, excluding ground state electronic interactions.⁶ The calculated half height band width (HHBW) increases as the oligomer chain increases, being 74, 84 and 116 nm for the 3QPV, 5QPV and 7QPV, respectively, and suggesting a larger number of conformers in the ground state as the length of the molecule increases. It is worth noting that, in particular, when spectra were obtained in spectroscopic grade chloroform, a drastic change of both the shape and wavelength towards the blue was observed and was time dependent. After many analyses, we discovered that the time dependent blue shift was due to bleaching produced by the amylene stabilizer contained in spectroscopic grade chloroform; this can be avoided by distilling the solvent and eliminating the amylene. The fluorescence spectra, Fig. 3, exhibit a main peak with a shoulder at higher wavelength; similarly to OPV excitonic emission features.9a The maximum in chloroform shifts from 476 nm for the 3QPV to 497 nm for both 5QPV and 7QPV; a few nanometers of difference is observed in THF

Table 1 Optical properties of the oligomers studied in this work in different solvents

	CHCl ₃					THF			Toluene						
Oligomer	λ_{Abs} (nm)	$\begin{array}{c} \epsilon \times 10^4 \\ \left(M^{-1} \ cm^{-1} \right) \end{array}$	Eg (eV)	$\lambda_{\rm Em}$ (nm)	E _{S10} (eV)	$\lambda_{\rm Abs}$ (nm)	$\begin{array}{c} \epsilon \times 10^4 \\ \left(M^{-1} \ cm^{-1} \right) \end{array}$	Eg (eV)	$\lambda_{\rm Em} \ ({\rm nm})$	E_{S10} (eV)	$\lambda_{ m Abs} \ (m nm)$	$\begin{array}{c} \epsilon \times 10^4 \\ \left(M^{-1} \ cm^{-1} \right) \end{array}$	Eg (eV)	$\lambda_{\rm Em}$ (nm)	E _{S10} (eV)
3C12DSB	388	3.2	2.80	440	2.93	389	3.2	2.82	437	2.94	388	3.1	2.81	438	2.93
3BrPV (3)	391	3.7	2.76	447	2.89	393	3.7	2.75	451	2.88	392	3.4	2.75	447	2.88
3QPV (6)	418	2.7	2.59	476	2.71	417	3.6	2.62	470	2.74	418	2.4	2.61	469	2.74
5QPV (7)	431	7.9	2.48	499	2.65	431	7.6	2.50	491	2.63	430	7.5	2.50	494	2.67
7QPV (11)	433	9.0	2.44	497	2.59	433	8.8	2.46	496	2.60	434	9.1	2.46	494	2.60

Table 2 Fluorescence quantum yield (ϕ), lifetime (τ), radiative (k_{rad}), non radiative (k_{nr}) rate constants and Stokes shifts ($\Delta \nu$) of the oligomers in different solvents

	CHCl ₃					THF						Toluene			
Oligomer	ϕ	τ (ns)	$k_{\rm rad}~({\rm ns^{-1}})$	$k_{\rm nr} ({\rm ns}^{-1})$	$\Delta \nu ({\rm cm^{-1}})$	ϕ	τ (ns)	$k_{\rm rad}~({\rm ns}^{-1})$	$k_{\rm nr} ({\rm ns}^{-1})$	$\Delta \nu (\mathrm{cm}^{-1})$	ϕ	τ (ns)	$k_{\rm rad}~({\rm ns}^{-1})$	$k_{\rm nr} ({\rm ns}^{-1})$	$\Delta \nu ~({\rm cm^{-1}})$
3C12DSB	0.76	1.51	0.50	0.16	3019	0.81	1.72	0.47	0.11	2857	0.90	1.51	0.59	0.06	2924
3BrPV (3)	0.27	1.26	0.21	0.58	3204	0.27	1.36	0.20	0.54	3272	0.32	1.24	0.26	0.45	3164
3QPV (6)	0.60	1.46	0.41	0.27	2793	0.53	1.68	0.31	0.28	2704	0.57	1.50	0.38	0.29	2579
5QPV (7)	0.64	1.28	0.50	0.28	2578	0.68	1.23	0.55	0.30	2215	0.62	1.07	0.58	0.35	2841
7QPV (11)	0.50	1.15	0.43	0.43	2193	0.56	0.98	0.57	0.45	2555	0.59	0.81	0.73	0.51	2433



Fig. 2 UV-Vis spectra and their corresponding molecular structure of the different oligomers studied in this work in chloroform.

and toluene. As for the optical band gap, this is more evident from the decrease of the first excited state energy, confirming that the effective conjugation length is already attained for the **5QPV**, Table 1. The excitation and absorption spectra are practically coincident; the Fig. 3 inset shows that of the **5QPV** in chloroform as an example. Moreover, it was found that the emission spectra are not affected by the excitation wavelength.⁶ These two latter results indicate that there is only one emitting state. The Stokes shift $(\Delta \nu)$ values are consistent with molecules that undergo a change from



Fig. 3 Fluorescence spectra of: dash dotted line **3C12DSB**, dashed line **3QPV**, solid line **5QPV**, and short dotted line **7QPV**. Inset: absorption (solid line) and excitation (dash-dotted line) spectra of **7QPV** in chloroform.

an aromatic to quinoid structure after excitation¹⁰ and they decrease with the conjugation, suggesting lower losses for internal conversion when passing from the 3QPV to the 7QPV. The HHBW of the emission spectra is of 58, 55, and 57 nm for the 3QPV, 5QPV and 7QPV, confirming that molecules are more planar in the excited state than in the ground state. Despite that, the higher fluorescence quantum yield (ϕ) is obtained for 5QPV (Table 2). In the particular case of the trimers, the highest quantum yield (0.76) is obtained for the hydrogen terminated trimer 3C12DSB, while the lowest (0.27) is for the 3BrPV. A similar behavior has been reported for phenyleneethynylene¹¹ type oligomers and attributed to the fact that bromine is an heavy atom that favors the triplet state formation, which actually can be seen from the lower radiative $(k_{\rm rad})$ constant of 0.21 ns⁻¹ with respect to the nonradiative rate constants (k_{nr}) of 0.58 ns⁻¹, Table 2. However, when quinoline is the terminal group, a slight quenching of the quantum yield emission is observed. This effect could be ascribed to the C=Nelectron withdrawing group that can produce a pathway for excitation state decay, which leads to a radiative constant greater than the nonradiative constant for this material.

Time correlated single photon counting measurements (TSCPC), Fig. 4, give a typical monoexponential decay for the three oligomers with lifetime τ decreasing from **3QPV** to **7QPV**. From ϕ and τ data, the radiative (k_{rad}) and nonradiative rate constants (k_{nr}) are calculated; with the exception of **5QPV** in chloroform, k_{rad} increases with the conjugation according to the Strickler–Berg expression.¹² The trend of the lifetime with *n* is mostly due to the corresponding increment of k_{nr} that is related to internal conversion and intersystem crossing. As previously observed, the losses due to internal conversion given by the Stokes shift go in the opposite way and is lower for **7QPV**.



Fig. 4 TCSPC data for: (\cancel{K}) **7QPV**, (\triangle) **5QPV**, (\bigcirc) **3QPV** and (\blacksquare) **3C12DSB** oligomers in toluene.

Thus, the major nonradiative decay pathway is expected to be intersystem crossing.

Cyclic voltammetry

Fig. 5 shows the first cycle of the voltammograms for each oligomer and Table 3 summarizes all the calculated electrochemical parameters. On the first anodic scan, two maxima oxidation peaks: E_{ox}^1 +1.53 V (irreversible) and E_{ox}^2 +2.03 V (quasi-reversible), are observed for **3QPV**, while in the cathodic scan two reduction peaks at E_{red}^1 -1.62 V (irreversible) and at E_{red}^2 -2.10 V (quasireversible) are also observed. The oxidation–reduction peaks are related to the loss of two electrons, but the irreversibility suggests that the resulting radical cations–anions are not electrochemically stable. In other words and according to the literature,¹³ the presence of more than one oxidative/reductive



Fig. 5 Voltammograms of $n \mbox{QPV}$ series in 0.1 M of $\mbox{Bu}_4 \mbox{NPF}_6$ in acetonitrile at a scan rate of 50 mV s^{-1}.

peak in the voltammograms of a conjugated molecule can be ascribed to the formation of polarons and bipolarons, or to the separate contribution of the different functional groups of the molecule,¹⁴ such as in this case, where the PV and the 2,5-bis(dodecanoxy) are electron donating groups, while quinolines are electron deficient groups. The oxidation potential of 3QPV is higher (+1.53 V) than that of trimers without quinolines, such as DSB (+0.96 V), 3C12DSB (+1.16 V) and 3BrPV (+1.29 V). However, the reduction potential of 3QPV is much lower (-1.62 V) than that of the references; DSB (-2.42 V), 3C12DSB (-2.35 V) and 3BrPV (-1.91 V). Certainly, the introduction of quinolines into the π -conjugated structure promotes sites for the reduction process, mainly because of the unbonded pairs of electrons of the nitrogen, in accordance with the reported work by Wang,² who found similar values for both sides of quinoline substituted trimers with 2,5-bis(methoxy) or phenyl or thiophenyl as central aryls. Actually, the redox potentials of such trimers in DCM at the onset are E_{ox} (irreversible) between +1.16 and +1.39 V, while E_{red} are between -1.35 and -1.57 V, with these results being consistent with those found for trimer 3QPV. However, as the phenylenevinylene conjugated chain increases to 5QPV and 7QPV, the maximal oxidation potential becomes similar for both oligomers: E_{ox} +1.17 V (quasi-reversible), but the reduction potentials increase, the longer the oligomer chain length is. This tendency is also consistent with the calculated electrochemical bands that are actually close to those calculated from absorption spectra gap (E_g) of 2.95, 2.79 and 2.77 eV for the 3QPV, 5QPV and 7QPV, respectively, and that is related to the more extended π -electron delocalization. It appears that the 5QPV and 7QPV behave more as OPV materials and that the influence of the quinolines is minimal; the quinoline effect is only reflected in shorter molecules as the trimers of ref. 2 and 3QPV.

Theoretical calculations

AM1 and DFT optimization. In order to better understand the optical and electrochemical properties of the oligomers and, in particular, to have a clearer idea of why the effective conjugation of the series is attained with **5QPV**, theoretical simulations were performed first on the trimers and then on the **nQPV** series. In this respect, we considered an all *trans* configuration for all the oligomers as was confirmed by NMR. After the DFT geometry optimization calculation, the trimer that shows a completely planar geometry is the **DSB** model, where all the atomic coordinates displayed a 0 Å value in *Z*-axis, meaning that all the atoms are positioned on the *X*,*Y* plane imparting an extended π -conjugation for this molecule.

Table 3 Electrochemical properties of oligomers studied in this work (0.5 mmol) in CH_2Cl_2 solution, 0.1 M Bu₄NPF₆, at a scan rate of 50 mV s⁻¹, (V vs. Ag/AgCl)

Oligomer	$E_{\mathrm{ox}}^{\mathrm{onset}}\left(\mathrm{V}\right)$	$E_{\mathrm{ox}}^{\mathrm{max}}\left(\mathrm{V}\right)$	$E_{\rm red}^{\rm onset}$ (V)	$E_{\rm red}^{\rm max}$ (V)	$E_{\mathrm{ox}}^{1/2}\left(V\right)$	$E_{\rm red}^{1/2}$ (V)	$HOMO^{1/2}$ (eV)	$LUMO^{1/2}$ (eV)	$E_{\rm g}~({\rm eV})$
DSB	0.63	0.96	-1.90	-2.42	0.80	-2.16	-5.09	-2.13	2.96
3C12DSB	0.98	1.16	-1.95	-2.35	1.07	-2.15	-5.36	-2.14	3.22
3BrPV (3)	1.11	1.29	-1.73	-1.91	1.20	-1.82	-5.49	-2.47	3.02
30PV (6)	1.38	1.53	-1.37	-1.62	1.46	-1.49	-5.75	-2.80	2.95
50PV (7)	1.05	1.17	-1.60	-1.77	1.11	-1.69	-5.40	-2.61	2.79
7QPV (11)	0.90	1.17	-1.66	-1.80	1.04	-1.73	-5.33	-2.56	2.77



In contrast, both 3C12DSB and 3BrPV trimers show that, while the 2,5-di(alkoxy) chains are in the same plane as that of the benzenoide, and upon increasing the conjugation by the electron donor character of the two oxygens, a dihedral angle of 27.5° and 27.67°, respectively, is formed. This angle is specifically formed between planes I (central di(alkoxy)benzene) and II and I and III, while that of II and III is of 0° .⁶ Interestingly, the dihedral angle displayed by **3QPV** is reduced to only 4.0° , Fig. 6. According to Wang,² who succeeded in obtaining single crystals of trimers related to 3QPV but without dialkoxy chains, the molecule is co-planar: (i) because of the π - π interactions that promote the formation of "bricks" of molecules, and (ii) because the nitrogen of the quinoline in 1-position that is out of the brick, interacts with the hydrogen in 8-position of the quinoline intermolecularly, which means with another brick of molecules. In contrast, 5QPV is a rather twisted structure, since the

phenylenevinylenes II and IV form an angle of 39° with respect to 2,5-di(alkoxy)benzene I, while this angle is of 44.6° between the vinylenequinolines III and V with respect to I. Interestingly, **7QPV** is a totally twisted structure with a pronounced dihedral angle of 63° between quinolines IV and VII with respect to I. The torsion is even more evident in Fig. 7 where the electrostatic potential is shown. The lack of planarity between the phenyl rings adjacent to the quinoline and those of the dialkoxy benzene I, as evidenced by the dihedral angles, explains the enormous influence that makes changes to the π -conjugation, and thus, to the electronic properties of this oligomer as determined by UV-Vis and fluorescence spectroscopy.

The molecular electrostatic potential (MEP). MEP predicted for the trimers⁶ and the **nQPV** series is shown in Fig. 7. In particular, the **DSB** trimer shows an homogeneous electron distribution map all along the phenylenevinylene chain, while **3C12DSB** and **3BrPV**



Fig. 7 Molecular electrostatic potential (MEP) in gas phase of **3QPV**, **5QPV** and **7QPV** oligomers.



Fig. 8 Frontier molecular orbitals; spatial distribution for the HOMO $\{-1\} \rightarrow$ LUMO and HOMO \rightarrow LUMO energy levels for the nQPV series obtained at the B3LYP/6-31G(d) level.

trimers show in addition negative regions in red color because of the oxygen unbounded pairs of electrons. Furthermore, in the **nQPV** series, it can be seen that both the oxygen of the dialkoxy chain as well as the nitrogen of the quinolines are surrounded by a great surface of negative charge, which can represent sites that are susceptible to redox potentials; in contrast, low electron density is located around hydrogen bonds. The determined MEP values for DSB, 3C12DSB, 3BrPV, 3QPV, 5QPV and 7QPV are -80.8, -137.2, -126.14, -179.1, -160.6 and -160.2 kJ mol⁻¹, respectively. Notice (i) that the less negative values are for the quinoline terminated oligomers, in particular for 3QPV followed by 5QPV that is almost the same as that of the 7QPV, and (ii) these values have the same trend to those found in the reduction potentials, where the 3QPV can be more easily reduced than the 5QPV and 7QPV. This could likely be associated to the fact that those groups that promote the push-pull effect (A-D-A) are closer in 3QPV, than for those in the other two oligomers that are separated by the π electron connectors (A- π -D- π -A) and that actually behave more like OPV materials.

Molecular orbitals. HOMO and LUMO energy conformations are depicted in Fig. 8 for the **nQPV** series. Sudeep *et al.*¹⁵ found that the high energy peak observed by UV-Vis for 2,5-di(alkoxy)phenyleneethynylene oligomers is generated by the HOMO{-1} \rightarrow LUMO transitions, because the 2,5-di(alkoxy) groups modify the central arene-ring's π -orbital through the resonance interaction with

the oxygens unshared electron pairs. This behavior is also observed for the 3QPV, where orbitals are located at the 2,5-bis(dodecanoxy)benzene, however, for 5QPV and 7QPV the HOMO $\{-1\}$ \rightarrow LUMO orbitals are rather localized at the phenylenevinylene segments, which could explain why the theoretical values decrease in energy from 0.88 to 0.5 and 0.29 eV for the 3QPV, 5QPV and 7QPV, respectively; that differs in magnitude but not in trend to the experimental values of 0.64, 0.52 and 0.46 eV, respectively, because of the more delocalized orbitals to the phenylenevinylene segments; this difference is not as marked between 5QPV and 7QPV. In general, it can be seen that the HOMO orbitals are localized mainly in the donor group of all compounds, except in the case of 3QPV where it is distributed in the 2,5-di(alkoxy) benzene-vinylene segment, whilst in both 5QPV and 7QPV, the HOMO orbitals are distributed all along the central phenylenevinylene segment, which in the case of 7QPV, the two external aryls on both sides of the quinoline do not show any spatial distribution. On the other hand, the LUMO orbitals are distributed all along the conjugated chain up to the nitrogen of the quinoline for 3QPV and 5QPV, but particularly, the distribution is not homogenous for 7QPV, which is located in the five phenylenevinylene segments without participation of the quinoline. It is worth noting that in the three cases, the aryls of the quinolines do not play an important electronic distribution, just the nitrogen. The theoretical HOMO-LUMO gap of 3.09, 2.84



Fig. 9 Experimental and fit Z-Scan data for **SQPV** at a concentration of 2.2×10^{-2} M and a laser intensity of 228 MW cm⁻². For this measurement a value of 0.39 cm GW⁻¹ was extracted for β from the fit data. An average value of 0.40 \pm 0.05 cm GW⁻¹ was extracted for measurements made at several intensities.

and 2.9 eV is very consistent with those found electrochemically, 2.95, 2.79 and 2.77 eV, for the series, which decreases as a function of the oligomer's length, due to the π -extended conjugation up to the effective conjugation attained with the **5QPV**.

Z scan measurements. The Z-scan was utilized to investigate the nonlinear parameters in the nQPV series. As a representative measurement, Fig. 9 shows that of 5QPV with the fit used to extract the nonlinear absorption coefficient. An average of the measured values β and σ for the **nQPV** series is shown in Table 4. These values have been extracted from the Z-scan measurements assuming both a Gaussian pulse width and spatial profile. It is to be pointed out that the excitation wavelength was chosen to be 1064 nm, instead of 532 nm, in order to avoid the linear absorption contribution that could be important in particular for 7QPV. The ns laser pulse can induce nonlinear optical and thermal effects, which are not distinguishable from one another in the ns regime. However, as no significant difference was observed in the nonlinear properties over an intensity range of 0.77 to 2.77 MW cm^{-2} , we can assume that free carrier and thermal effects are minimal.

It can be seen that σ increases with an increased conjugation length of the molecules. This behavior has been observed in other molecular systems, and has been attributed to an increased dipole moment that typically accompanies the increased conjugation length.¹⁶ Despite the fact that the concentration of **7QPV** is less than that of the other two molecular systems studied, the value of σ can be compared, as it should be independent of the concentration (this is not the case for comparing the values of β). The measured two-photon absorption cross-section for 7QPV is expected to be significantly larger than that for 3QPV and 5QPV due to its increased conjugation length and the corresponding shift in the linear absorption shown in Fig. 2. In fact, due to the red-shifted linear absorption spectrum of 7QPV, compared to the spectra of the other molecules, the two-photon absorption for 1064 nm light is in resonance with the HOMO-LUMO transition, whereas in the case of 3QPV and 5QPV absorption at 1064 nm is towards the lower energy side of the resonance. This could also explain the difference in the value range measured for this

Table 4 Measured values of the nonlinear absorption coefficient β and the two photon absorption cross-section σ for the **nQPV** series. These values are used as a relative comparison between samples

Oligomer	Concentration (M)	β (CM/GW)	σ (cm ⁴ × s per photon × molecule)
3QPV (6) 5QPV (7) 7QPV (11)	$\begin{array}{c} 2.2 \times 10^{-2} \\ 2.2 \times 10^{-2} \\ 1.1 \times 10^{-4} \end{array}$	$egin{array}{c} 0.18 \pm 0.06 \ 0.40 \pm 0.05 \ 0.14 \pm 0.02 \end{array}$	$\begin{array}{c} 2.48 \pm 0.8 \times 10^{-48} \\ 5.68 \pm 0.7 \times 10^{-48} \\ 4.04 \pm 0.7 \times 10^{-46} \end{array}$

family with respect to other phenylenevinylenes, in which there is a two photon absorption resonance contribution.¹⁷

Conclusions

The ¹H *I*-resolved (IRES) 2D NMR spectroscopy is a method to unambiguously identify the E isomer in OPV type oligomers that usually present a high signal density in the aromatic-vinyl region. Our investigation of OPV oligomers bearing quinolines at both extremities disclosed that: (1) effective conjugation is attained with the 5QPV as was demonstrated by UV-Vis and fluorescence spectroscopies, (2) 7QPV is not more conjugated than 5QPV because the largeness of the molecule leads to torsion of the phenylenevinylene structure, reducing the degree of conjugation as was determined by theoretical calculations, (3) a possible push-pull effect is clear only for the trimer 3QPV, where the 2,5-di(dodecanoxy) donor groups are close to the quinoline electron deficient groups, while for 5QPV and 7QPV no considerable effect of the quinolines was observed either spectroscopically, electrochemically or theoretically, (4) the HOMO orbitals are localized mainly in the 2,5-di(dodecanoxy)benzene donor group of the trimer **3OPV**, but in the three central phenylenevinylene groups of the 5QPV and 7QPV oligomers, while the LUMO orbitals are distributed all along the conjugated chain up to the nitrogen of the quinoline.

Experimental section

General

The following chemical reagents: 4-bromobenzaldehyde, 2-quinolinecarboxaldehyde, methyltriphenylphosphonium bromide (MTPP-Br), potassium *tert*-butoxide (*t*-BuOK), palladium(II) acetate, tri-*o*-tolylphospine (POT), anhydrous sodium acetate, and tetrabutylammonium bromide ($^{-}Br^{+}NBu_{4}$) were purchased from Aldrich and used without further purification. Electrochemical grade tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) was purchased from Fluka. DMF, CHCl₃, CH₂Cl₂ and hexanes were purchased from J. T. Backer. Triethylamine (Et₃N) (Aldrich) was distilled from KOH, THF was first distilled from KOH and then from sodium benzophenone until a typical blue complex was formed. Acetonitrile was passed through a plug of silica gel and then distilled from NaH. All solvents used for optical characterization were of spectroscopic grade and obtained from Aldrich.

Theoretical studies

All calculations were performed using the Spartan10 and Gaussian 09W programs. Lateral propoxy chains were used in place of the

dodecanoxy chains in order to shorten the computational time; this approximation is usually accepted.¹⁵ Optimization of the geometry of the structures was carried out by AM1 semiempirical calculations. The coordinates thus obtained were further optimized through density functional theory (DFT) calculations at the restricted B3LYP (Becke 3-parameters Lee– Yang–Parr exchange correlation function) level with a 6-31G(d) mixed basis set.

Equipment

¹H (300 MHz), Homo-J-Resolved, DEPT-135, APT, and ¹³C NMR (75.4 MHz) spectra were recorded at room temperature on a Jeol Eclipse spectrometer using CDCl₃ as solvent and internal reference. FAB+ mass spectra were recorded on a JEOL JMS AX505 HA instrument. Optical properties were studied in spectroscopic grade THF, toluene and chloroform (Aldrich). UV-Vis spectra were recorded on a Shimadzu 2401PC and on an Agilent 8453 spectrophotometer in the 200-1100 nm range. Band gaps (E_{α}) were obtained at the onset of the normalized UV-Vis spectra (absorbance of 0.1). Static fluorescence studies were performed on a Perkin Elmer LS50B spectrometer. Emission spectra were obtained by exciting at 10 nm before the maximum absorption spectra, while excitation spectra were obtained by fixing the maximum emission wavelength. Fluorescence quantum yield was obtained according to ref. 18 and by using quinine sulfate in 0.1 M H₂SO₄ as standard. Measurements were performed by controlling the temperature at 25.0 \pm 0.3 °C using a water circulating bath. Values were averaged from four samples. The first excited state energy (E_{S10}) was calculated from the wavelength at which the normalized absorbance and fluorescence spectra cross. Lifetime τ was obtained by a single photon counting technique (10000 counts) in a Horiba TemPro instrument at 370 nm NanoLED excitation (1 MHz repetition rate) and by using a 0.01% ultrapure water dispersion of Ludox AS40 (Aldrich) for the prompt signal. The electrochemical properties of oligomers were investigated by cyclic voltammetry in a C3 cell stand from Basi coupled to a potentiostat/galvanostat ACM Gill AC. All the experiments were performed at room temperature in acetonitrile containing Bu_4NPF_6 (0.1 M) as the supporting electrolyte, glassy carbon as a working electrode (GCE), Pt wire electrode as the counter electrode, Ag/AgCl electrode as the reference electrode and ferrocene/ferrocenium (FOC) as internal reference ($E_{ox} = 5.1$ V, $E_{\rm red}$ = 3.05 V); value of -4.8 eV below the vacuum level. The experiments were carried out under a nitrogen atmosphere at a scanning rate of 50 mV s⁻¹ between -3.0 and +3.0 V. In all the experiments a redox signal was detected at ~ -0.8 V, which was assigned to the electrolyte solution. The molecular orbital energies HOMO and LUMO were calculated from the first oxidation $(E_{\rm ox})$ and reduction $(E_{\rm red})$ potentials using the relationship:¹⁹ $E^{\text{HOMO[LUMO]}} = \left[-\exp(E_{1/2(\text{Ox[red]}\nu\text{s.Ag/AgCl})} - E_{\text{onset}(\text{FOC}\nu\text{s.Ag/AgCl})}\right] - E_{\text{onset}(\text{FOC}\nu\text{s.Ag/AgCl})}$ 4.8. In our electrochemical experiments, ferrocene exhibited an (E) oxidation potential of 0.51 V. The electrochemical energy gap (E_g) was the difference between LUMO-HOMO. The open aperture Z-scan can be used to measure the nonlinear absorption coefficient and two-photon absorption cross-section.¹⁷

This method was utilized to investigate these nonlinear parameters in the **nQPV** molecule series using a q-switched YAG:Nd laser with a pulse width of 15 ns (at 1064 nm). For **3QPV** and **5QPV** in THF a concentration of 2.2×10^{-2} M is used. For **7QPV**, the concentration was 1.08×10^{-4} M due to the saturation limit of the solvent; therefore, a comparison with the other molecular systems cannot be directly made. The sample length was 1 cm; this path length was chosen in order to obtain a detectable signal in the weakest sample of the three samples (**3QPV**). For each material, the nonlinear absorption is measured at several input intensities between 0.77 to 2.77 MW cm⁻².

Synthesis

1,4-Bis((E)-4-bromostyryl)-2,5-bis(dodecyloxy) benzene 3 (3BrPV). A mixture of 1,4-bis(dodecanoxy)-2,5-diiodo-benzene 1 (1000 mg, 14.32×10^{-2} mmol), Pd(OAc₂) (32 mg, 0.14 mmol), anhydrous sodium acetate (352 mg, 4.29 mmol) and ⁻Br⁺NBu₄ (461 mg, 1.43 mmol) were placed in a two neck round bottom flask. Then, 20 mL of degassed Et₃N were added via a cannula, stirred and heated for 1 h. Later, 4-bromostyrene 2 (524 mg, 2.86 mmol) dissolved in 80 mL of DMF (previously bubbled with nitrogen for 15 min) was added dropwise (very important) and heated at 130 °C for 72 h. After removing the solvents, the crude product was washed with a solution of H2O-NaHCO3, then the organic phase was extracted with CHCl3 and the solvent evaporated. The crude product was taken up in 3 mL of CHCl₃ and precipitated twice in methanol. The resulting product was purified: (1) in a SiO₂ column first using hexane to eliminate the remaining 1 and then by a mixture of hexane: CH_2Cl_2 (3:1 v/v, $R_f = 0.4$) and (2) by preparative GPC chromatography (Biorads, Bio-beds SX1, toluene) to afford a yellow fluorescent powder in 70% yield. m.p. = 95-105 °C. ¹H NMR (CDCl₃, 300 MHz): δ (ppm) 7.46(d, 4H, J = 8.35 Hz, Ar-H1), 7.44(d, 2H, J = 16.51 Hz, ==CH4), 7.37(d, 4H, J = 8.80 Hz, Ar-H2), 7.08(s, 2H, Ar-H5), 7.05(d, 2H, J = 16.51 Hz, =CH3), 4.03(t, 4H, J = 6.46 Hz, CH₂- α -O), 1.85(m, 4H, CH₂- β -O), 1.52(m, 4H, CH₂-γ-O), 1.25(br s, 32H,-CH₂-), 0.87(t, 6H, CH₃). ¹³C NMR (CDCl₃, 75 MHz): δ(ppm) 151.22, 136.98, 131.84, 128.05, 127.74, 126.82, 124.29, 121.19, 110.73, 69.62, 32.02, 29.77, 29.55, 29.47, 26.38, 22.79, 14.23. UV-Vis (CHCl₃); λ_{max} (330 nm) ε (5.11 \times 10⁴ M⁻¹ cm⁻¹), (394 nm) ε (6.75 × 10⁴ M⁻¹ cm⁻¹).

2-Vinyl-quinoline 5. A mixture of 2-quinolinecarboxaldehyde 4 (1 g, 6.36 mmol) and methyltriphenylphosphonium bromide (2.5 g, 6.97 mmol) in dry THF (40 mL) was stirred at 0 °C for 15 min under Ar. Then, t-BuOK (0.78 g, 6.97 mmol) was added in portions and the reaction was stirred at room temperature for 24 h. After this time, 50 mL of water was added and the organic layer extracted twice with CH₂Cl₂. The combined organic layers were washed twice with water, dried over anhydrous Na₂SO₄ and the solvent evaporated under vacuum. The resulting crude product was purified using a neutral alumina chromatographic column using hexane as eluent to obtain a yellow oil in 75% yield. ¹H NMR (CDCl₃, 300 MHz): δ (ppm) 8.06(dd, 1H, J = 9.08 Hz, QnH8), 8.03(dd, 1H, J = 8.80 Hz, QnH5), 7.71(d, 1H, J = 7.98 Hz, QnH4), 7.65(t, 1H, J = 6.80 Hz, QnH7), 7.54(d, 1H, J = 8.53 Hz, QnH3), 7.44(t, 1H, J = 7.153 Hz, QnH6), 7.00(q, 1H, =C-HC), 6.23(d, 1H, J = 17.61 Hz, =C-HB),

5.62(d, 1H, J = 10.73 Hz, =C-HA). ¹³C NMR (CDCl₃, 75 MHz): δ (ppm) 156.52, 146.21, 136.54, 132.80, 130.11, 128.92, 127.91, 126.82, 120.0, 118.73.

2,2'-(1E,1'E)-2,2'-(2,5-Bis(dodecanoxy)-1,4-phenylene)bis(ethene-2,1-diyl)bisquinoline 6 (3QPV). A mixture of 5 (50 mg, 0.322 mmol), 1,4-bis(dodecanoxy)-2,5-diiodo-benzene 1 (110 mg, 0.161 mmol), Pd(OAc₂) (3 mg, 0.0135 mmol), and POT (7 mg, 0.023 mmol) in Et₃N:DMF (80:20 mL) was stirred under Ar at reflux for 72 h. After cooling, the resulting mixture was filtered and the solvent evapored. The orange residue was taken up in CHCl₃ (100 mL). The organic layer was washed with water (100 mL), dried with Na₂SO₄, filtered, and evaporated to dryness. The resulting residue was purified by column chromatography by using neutral alumina and hexane-CHCl₃ (8:2 v/v) as eluent to afford an orange powder in 78% yield. m.p. = 87-90 °C. ¹H NMR $(CDCl_3, 300 \text{ MHz}): \delta(ppm). 8.05(d, 2H, J = 8.53 \text{ Hz}, QnH8),$ $8.004(d, 2H, J = 16.5 \text{ Hz}, -C = H_B), 7.75(2d, 4H, QnH5, H4),$ QnH3), 7.46(d, 2H, J = 16.23 Hz, -C=H_A), 7.29(s, 2H, Ar-H), $4.06(t, 4H, J = 6.60 \text{ Hz}, CH_2-\alpha-O), 1.90(q, 4H, J = 6.88 \text{ Hz},$ $CH_2-\beta-O$, 1.56(q, 4H, $CH_2-\gamma-O$), 1.24(br s, 32H,-CH₂-), 0.86(t, 6H, CH₃). ¹³C NMR (CDCl₃, 75 MHz): δ(ppm) 156.73, 151.47, 148.29, 136.24, 129.75, 129.59, 129.18, 128.97, 127.57, 127.35, 127.03, 126.16, 118.67, 110.52, 69.47, 32.03, 29.78, 29.61, 29.56, 29.48, 26.36, 22.79, 14.22. UV-Vis (CHCl₃); λ_{max} (418 nm), ε (2.7 \times 10⁴ M⁻¹ cm⁻¹). MALDI-TOF (M^{•+}): *m/z* calcd for C52H68N2O2: 752.53, found, 752.44.

2,2'-(1E,1'E)-2,2'-(4,4'-(1E,1'E)-2,2'-(2,5-Bis(dodecanoxy)-1,4phenylene)bis(ethene-2,1-diyl)bis(4,1-phenylene))bis(ethene-2,1diyl)diquinoline 7 (5QPV). A mixture of 3 (300 mg, 0.37 mmol), 5 (173 mg, 1.11 mmol), Pd(OAc₂) (8 mg, 0.03 mmol), anhydrous sodium acetate (73 mg, 0.89 mmol), and ⁻Br⁺NBu₄ (48 mg, 0.149 mmol) in DMF: Et₃N (90:10 mL) was stirred under N₂ and heated at 130 °C for 72 h. After cooling, 100 mL of H₂O-NaHCO₃ was added and the organic phase was extracted with CHCl₃, then dried with MgSO₄, filtered and the solvent evaporated under reduced pressure. The resulting residue was dissolved in 1 mL of CHCl₃ heated until its total dissolution and precipitated in methanol three times. The desired product was obtained as an orange solid in 60% yield. m.p. = 155–163 °C. ¹H NMR (CDCl₃, 300 MHz): δ (ppm). 8.09(2d, 2H, I = 8.80 Hz, QnH8), 8.08(d, 2H, J = 8.80 Hz, QnH5), 7.98(d, 2H, J = 7.98 Hz, QnH4), 7.71(2t, 4H, *J* = 8.5 Hz, QnH6, H7), 7.68(d, 2H, *J* = 16.23, -C=H_B), 7.66(d, 4H, *J* = 8.53 Hz, Ar–H10), 7.62(d, 2H, *J* = 9.90 Hz, QnH3), 7.55(d, 4H, J = 8.25 Hz, Ar–H9), 7.53(d, 2H, J = 16.51, –C=H_D), 7.42(d, 2H, $J = 16.23, -C = H_A$, 7.15(d, 2H, $J = 15.68, -C = H_C$), 7.13(s, 2H, Ar-H), $4.06(t, 4H, J = 6.60 \text{ Hz}, CH_2 - \alpha - O), 1.89(q, 4H, J = 6.88 \text{ Hz}, CH_2 - \beta - O),$ 1.56(q, 4H, CH₂-γ-O), 1.25(br s, 32H,-CH₂-), 0.86(t, 6H, CH₃). ¹³C NMR (CDCl₃, 75 MHz): δ(ppm) 156.09, 151.29, 148.26, 138.56, 136.52, 135.67, 134.33, 131.00, 129.92, 129.16, 128.90, 128.55, 128.40, 127.70, 127.61, 127.41, 127.03, 126.28, 124.12, 119.37, 110.71, 69.65, 32.04, 29.80, 29.60, 29.50, 26.43, 22.80, 14.23. UV-Vis (CHCl₃); λ_{max} (435 nm), ϵ (7.9 × 10⁴ M⁻¹ cm⁻¹). MALDI-TOF (M^{•+}): *m/z* calcd for C68H80N2O2: 956.62, found, 956.58.

(*E*)-4-(2-(Quinolin-2-yl)vinyl)benzaldehyde 9. A mixture of 2-vinyl-quinoline 5 (1.84 g, 11.88 mmol), 4-bromobenzaldehyde

8 (2 g, 10.88 mmol), Pd(OAc₂) (7.27 mg, 0.324 mmol), and POT (664 mg, 0.54 mmol) in Et₃N: THF (56: 14 mL) was stirred under Ar at reflux for 48 h. After cooling, the resulting mixture was filtered and the solvent evaporated. The residue was taken up in $CHCl_3$ (150 mL). The organic layer was washed with water (100 mL), dried with Na₂SO₄, filtered, and evaporated to dryness. The resulting residue was purified by column chromatography by using neutral alumina and hexane-CH₂Cl₂ (1/1 v/v, $R_f = 0.3$) as an eluent to obtain a pale yellow powder in 76% yield. m.p. = 108–112 $^{\circ}$ C. ¹H NMR (CDCl₃, 300 MHz): δ (ppm) 10.0(s, 1H, CHO), 8.13(dd, 1H, J = 8.5 Hz, QnH8), 8.07(dd, 1H, J = 8.5 Hz, QnH5), 7.87(d, 1H, J = 8.5 Hz, Ar-H10),7.86(d, 1H, J = 6.05 Hz, QnH4), 7.76(dt, 2H, J = 8.25 Hz, QnH7, H6), 7.72(d, 1H, J = 16.23 Hz, $-C = CH_B$), 7.64(d, 1H, J = 8.5 Hz, Ar-H9), 7.52(d, 1H, J = 7.15 Hz, QnH3), 7.51(d, 1H, J = 16.23 Hz, -C=CH_A). ¹³C NMR (CDCl₃, 75 MHz): δ (ppm) 191.67, 155.12, 148.28, 142.52, 136.69, 136.04, 132.92, 132.15, 130.30, 130.06, 129.37, 127.73, 127.66, 126.71, 119.67. UV-Vis (CHCl₃); λ_{max} (295 nm) ε $(1.73 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1})$, (344 nm) ε (3.04 \times 10⁴ M⁻¹ cm⁻¹) (356 nm) ε (2.94 × 10⁴ M⁻¹ cm⁻¹).

(E)-2-(4-Vinylstyryl)quinoline 10. A mixture of 9 (1 g, 3.86 mmol) and methyltriphenylphosphonium bromide (1.6 g, 4.26 mmol) in dry THF (50 mL) was stirred at 0 °C for 15 min under N2. Then, t-BuOK (0.5 g, 4.26 mmol) was added portion wise and the reaction was stirred at room temperature for 24 h. After this time, 50 mL of water were added. The organic phase was extracted twice with CH₂Cl₂. The combined organic layers were washed with water, dried over anhydrous Na₂SO₄, filtered and the solvent vacuum evaporated. The resulting residue was purified by column chromatography by using neutral alumina and hexane-CH2Cl2 (5/5 v/v) as an eluent to obtain a pale yellow solid in 88% yield. m.p. = 112-116 °C. ¹H NMR $(CDCl_3, 300 \text{ MHz}): \delta(ppm) 8.12(d, 1H, J = 8.5 \text{ Hz}, QnH8), 8.09(dd, 1H, J = 8.5 \text{ Hz})$ 1H, J = 8.5 Hz, QnH5), 7.78(dd, 1H, J = 8.25 Hz, QnH4), 7.69(t, 1H, J = 8.8 Hz, QnH7), 7.64(d, 1H, J = 17.33 Hz, -C=CH_B), 7.61(t, 1H, J = 8.25 Hz, QnH6), 7.49(dd, 1H, J = 7.15 Hz, QnH3), 7.42(d, 4H, J = 8.25 Hz, Ar-H), 7.40(d, 1H, J = 16.51 Hz, -C=CH_A), 6.72(q, 1H, -C=CH_C), 5.79(d, 1H, J = 17.61 Hz, -C=CHD), 5.28(d, 1H, J = 10.73 Hz, -C==CH_E). ¹³C NMR (CDCl₃, 75 MHz): δ(ppm) 156.01, 148.33, 137.96, 136.48, 136.41, 136.13, 134.09, 129.85, 129.26, 128.93, 127.60, 127.42, 126.77, 126.25, 119.37, 114.42. UV-Vis (CHCl₃); λ_{max} (294 nm) ϵ (2.97 × 10⁴ M⁻¹ cm⁻¹), (346 nm) ϵ (4.89 × 10⁴ M⁻¹ cm⁻¹) (359 nm) $\epsilon (4.84 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}).$

Compound 11 (7QPV). A mixture of 3 (235 mg, 0.291 mmol), **10** (225 mg, 0.874 mmol), Pd(OAc₂) (14 mg, 0.058 mmol), anhydrous sodium acetate (72 mg, 0.874 mmol), and $^-Br^+NBu_4$ (94 mg, 0.292 mmol) in DMF:Et₃N (90:10 mL) was stirred under N₂ and heated at 130 °C for 72 h. After cooling, 100 mL of H₂O-NaHCO₃ was added and the organic phase was extracted with CHCl₃, dried with MgSO₄, filtered and the solvent evaporated under reduced pressure. The resulting residue was dissolved in 1 mL of CHCl₃, heated until total dissolution and precipitated in methanol three times. Later, the residue was re-dissolved in 5 mL of hot toluene and left standing until the desired product precipitated during two days; it was then filtered and dried. The desired product was obtained as a deep orange solid in 47% yield. m.p. = 175–182 °C. ¹H NMR (CDCl₃, 300 MHz): δ (ppm) 8.15(d, 2H, *J* = 8.08 Hz, QnH8), 8.12(d, 2H, *J* = 8.08 Hz, QnH5), 7.78(dd, 2H, J = 8.16 z, QnH4), 7.71(2t, 4H, J = 8.40 Hz, QnH7, H6), 7.72(d, 2H, J = 16.5, $-C = H_A$), 7.66(d, 2H, J = 8.71 Hz, Ar–H11), 7.64(d, 2H, J = 8.4 Hz, QnH3), 7.54(d, 4H, J = 8.56 Hz, Ar–H12), 7.49(d, 2H, J = 16.46, $-C = H_E$), 7.46(d, 2H, J = 8.6 Hz, Ar–H10), 7.42(d, 2H, J = 17.60, $-C = H_E$), 7.37(d, 2H, J = 6.40 Hz, Ar–H9), 7.17(d, 2H, J = 16.0 Hz, $-C = H_D$), 7.13(d, 2H, J = 16.53 Hz, $-C = H_C$), 7.14(s, 2H, ArO–H13), 7.05(d, 2H, J = 16.30 Hz, $-C = H_F$), 4.06(t, 4H, J = 6.60 Hz, $CH_2-\alpha-O$), 1.89(q, 4H, J = 6.88 Hz, $CH_2-\beta O$), 1.56(q, 4H, $CH_2-\gamma-O$), 1.25(br s, 32H, $-CH_2-$), 0.86(t, 6H, CH_3) UV-Vis ($CHCl_3$); λ_{max} (440 nm), ε (19.5 × 10⁴ M⁻¹ cm⁻¹). MALDI-TOF (M^{•+}): m/z calcd for C80H92N2O2: 1160.72, found, 1160.76.

1,4-Bis(dodecanoxy)-2,5-distyrylbenzene, model compound 12⁸ (3C12DSB). A mixture of 1,4-bis(dodecanoxy)-2,5-diiodo-benzene 1 (550 mg, 0.787 mmol), Pd(OAc₂) (7 mg, 0.031 mmol), and tris-(o-toly1)phosphine (10 mg, 0.031 mmol) were placed in a two neck round bottom flask. Then 20 mL of Et₃N-DMF (1:4 v/v) were added via a cannula, stirred and heated for 1 h. Later, freshly distilled styrene (172 mg, 0.19 mL, 1.65 mmol) dissolved in 5 mL of DMF (previously bubbled with nitrogen for 15 min) was added and heated at 120 °C for 72 h. After removing the solvents, the crude product was washed with brine solution, then the organic phase was extracted with CH₂Cl₂, dried over MgSO₄ and the solvent evaporated. The crude product was purified by preparative GPC chromatography (Biorads, Bio-beds SX1, toluene) and then recrystallized in hexane to afford a pale orange powder in 78% yield. m.p. = 75–78 °C. ¹H NMR $(CDCl_3, 300 \text{ MHz}): \delta(ppm) 7.54(dd, 4H, I = 7.15 \text{ Hz}, Ar-H), 7.50(d, 4H, I = 7.15 \text{ Hz}, Ar-H$ 2H, J = 16.51 Hz, ==CH-), 7.38(t, 4H, J = 7.70 Hz, Ar-H), 7.26(m, 2H, J = 7.43 Hz, Ar-H), 7.15(d, 2H, J = 16.51 Hz, ==CH-), 7.14(s, 2H, Ar-H), 4.07(t, 4H, J = 6.46 Hz, CH₂- α -O), 1.89(m, 4H, CH₂- β -O), 1.56(m, 4H, CH₂- γ -O), 1.28(br s, 32H,-CH₂-), 0.89(t, 6H, CH₃).

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