Dyes and Pigments 133 (2016) 41-50



Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

Synthesis and photophysical properties of highly fluorescent 2-aryl-6-(aryleneethynylene)-1*H*-indoles



PIGMENTS

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ARTICLE INFO

Article history: Received 14 December 2015 Received in revised form 1 March 2016 Accepted 13 May 2016 Available online 24 May 2016

Keywords: Arylindoles Intense fluorescence Quantum yield Solvatofluorochromism Cyclic voltammetry

1. Introduction

ABSTRACT

Nine novel 2-aryl-6-(aryleneethynylene)-1*H*-indoles were prepared by one pot Sonogashira crosscoupling in DMSO and fluoride promoted cyclization followed by N-alkylation. The photophysical properties of these compounds are described. Absorption and excitation spectra of these compounds were independent of the solvent polarity, while their emission spectra showed a pronounced dependence. Fluorescence quantum yields in solution were very high and decreased with solvent polarity; possible processes that account for excessive values of φ are discussed. Cyclic voltammetry studies indicate irreversible redox processes and DFT calculations suggest they occur in the indole segment. © 2016 Elsevier Ltd. All rights reserved.

Indoles are privileged structures because of their ubiquity in natural products and wide span of biological activity. In addition, indoles are unsaturated, electron rich compounds capable to display physical properties with great potential for many different applications. Fluorescent indole derivatives are common structures used for the design of fluorescent probes for a myriad of analytical applications [1–4]. Some of these compounds display nonlinear optics and have served to prepare two photon fluorescent probes [5] for cellular imaging and even used for photothermal ablation of cancer cells [6,7]. Indole-derived compounds may also display photochromism [8,9] and electroluminescence [10] and thus have potential for application in optoelectronic materials and solar cells [11]. These remarkable properties of indole derivatives prompted us to start our own studies aimed to obtain highly fluorescent small conjugated molecules. Based on the known high fluorescence of 2-

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arylindoles [12], we set out to prepare derivatives with an additional structural group that could expand the conjugated system and modify its properties, and the arylalkyne moiety was chosen for its well documented participation in aryleneethynylene (AE) chromophores of high quantum yield [13,14]. This led to the preparation of 2-aryl-6-(aryleneethynylene)-1*H*-indoles of type **1** and herewith we report on the synthesis, photophysical and electronic properties of these novel, highly fluorescent compounds (Scheme 1).

2. Experimental

2.1. Synthesis

Full experimental details for preparation of all of the compounds involved in this study, spectroscopic characterization data and selected NMR spectra can be found in the supplementary information.

2.2. Theoretical calculations

All calculations were performed with Spartan 14 v.1.1.2



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(Wavefunction. Inc). First the equilibrium conformer at ground state was found at AM1 level and then this geometry was further optimized through Density Functional Theory (DFT) calculations at the restricted B3LYP level with 6-31G(d) basis set. The coordinates generated during the DFT optimization processes were used as input for the electronic excited state calculations and the first six singlet electronic excited states were calculated by TDDFT with the same basis set and in vacuum. The UV/Vis spectra were calculated by running a single point TDDFT calculation using the Tamm-Dancoff Approximation (TDA). By default only pairs of filled/unfilled orbitals which have amplitudes larger than 0.15 are considered.

2.3. Photophysical properties

The photophysical characterization was carried out in spectroscopic grade CH₂Cl₂, DMSO and toluene from Aldrich. UV-Vis absorption spectra were measured on a Shimadzu 2401PC spectrophotometer. Optical band gap (*E*g_{opt}) was determined from the intercept with the X axis of the tangent of the absorption spectrum drawn at absorbance of 0.1. Stokes shift (Δv) was determined as the difference between the lower energy absorption and higher energy emission bands in wavenumbers. Emission and excitation spectra have been recorded with a Perkin-Elmer LS 50B spectrofluorometer. Excitation spectra were obtained by fixing the maxima of fluorescence as the emission wavelength. Fluorescence quantum yields in solution (ϕ) were determined according to the reported procedure [15] using quinine sulphate in H₂SO₄ 0.1 M $(\phi = 0.54 \text{ at } 310 \text{ nm})$ as the standard. The excitation wavelength was 10 nm lower than the absorption maximum. Measurements were carried out by controlling the temperature at 25.0 \pm 0.5 °C with a water circulating bath. Three solutions with absorbance at the excitation wavelength lower than 0.1 were analyzed for each sample and the quantum yield was averaged. Lifetimes were obtained by TCSPC (Time-correlated single photon counting) with a Tempro Horiba equipment with 370 nm nanoLEDs. 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 [1,4-Bis(4-methyl-5-phenyl-2-oxazolyl)benzene] methanol solution (optical density <0.1 and lifetime of 0.93 ns [16]). Data were fit in the software DAS6 available in the equipment.

2.4. Electrochemical studies

The electrochemical properties of all of the compounds were investigated by cyclic voltammetry in a C3 Stand cell from Basi, coupled to an ACM Gill AC potentiostat/galvanostat. The system consisted in a conventional three-electrode cell: platinum or glassy 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 and ferrocene/ferrocenium (FOC) as internal reference (Eox = 0.58 V, Ered = 0.701 V); a value of -4.8 eV below the vacuum level was considered. Voltammetric measurements were performed at room temperature in CH₂Cl₂ containing Bu₄NPF₆ (0.1 M) as the supporting electrolyte. Prior to recording the voltammograms, all of the solutions (~0.5 mmol) were



Scheme 1. 2-aryl-6-(aryleneethynylene)-1H-indoles.

deoxygenated by bubbling nitrogen at least for 15 min. The experiments were carried out under nitrogen atmosphere at a scanning rate of 50 mV/s. The molecular orbital energies HOMO and LUMO were calculated from the first oxidation (*E*ox) and reduction (*E*red) potentials with the relationship [17,18] *E* HOMO (LUMO) = [-e(Emax (Ox[red] vs. Ag/AgCl)]-4.8.

3. Results and discussion

3.1. Synthesis

The synthesis of the target indole compounds **1a-i** was envisaged as a straightforward sequence of Sonogashira couplings between the arylcarbamates **2** or **5** [19] with arylalkynes **3a-g**, followed by cyclization and *N*-alkylation (Scheme 2). This synthetic strategy could be applied to obtain even more conjugated molecules if an arylethynylene oligomer is used as the arylalkyne 3 in Scheme 2.

Carbamate **2** allowed introduction of identical aryl groups by Sonogashira coupling, while carbamate **5** made possible the sequential introduction of different aryl groups through a regioselective coupling at the C–I bond [19], followed by a second coupling at the C–Br bond [20]. Substituents R¹ and R³ on the aryl groups were designed to modulate electronic donation/withdrawal on these molecules and the *N*-alkylation step was deemed necessary to make these compounds soluble in organic solvents (i.e. these compounds are soluble in toluene, dichloromethane and DMSO as representative common organic solvents of different polarity). The attempted *N*-alkylation of indoles **1g** and **1h** containing carbonyl groups, showed extensive decomposition under experimental conditions and consequently these less soluble, free NH indoles were studied as such.

3.2. Theoretical calculations

All of the compounds **1a-i** synthesized and studied in this work are depicted in Scheme 3, they share the same general structure, where a central indole is conjugated to an aryleneethynylene at the C-6 position and to a phenyl group at C-2, variations in their structure include the substituents on the aryl groups and the indole *N*-substituent. The structural modulation obtained by changing these substituents affected properties such as geometry at the ground state, dipole moment, molecular orbitals, and excitation energies as shown below.

3.2.1. Geometry at the ground state

For sake of discussion, Fig. 1 shows the optimized geometry of **1a** as example of the series, where the aryl units have been labelled according to the planes they form. Three planes can be visualized: plane I of the aryleneethynylene segment, plane II of the indole and plane III belonging to the phenyl directly attached to the indole. Table 1 displays all the calculated dihedral angles, where α is the dihedral angle between plane I and II (considering atoms C3, C5, C10 and C16 in Fig. 1) and β is the dihedral angles between planes II and III (considering atoms C13, N, C18 and C22 in Fig. 1). We observed that α is close to 0°, indicating that the indole is almost coplanar with the aryleneethynylene segment; this supported the assumption that this part of the molecule is highly conjugated. On the contrary, a larger deviation from zero is observed for the dihedral angle β between planes II and III; for instance, molecules 1f and 1g for which \mathbb{R}^3 is hydrogen have a dihedral angle β of around 27° and the rest, for which R³ is a hexyl group, exhibit a larger distortion with β being around 50° due to steric repulsion between the *N*-



Scheme 3. Chemical structure of indoles 1a-i bearing different electron donor and withdrawing groups synthesized and studied in this work.

hexyl and C-2 aryl group. This means that at the ground state, the equilibrium conformer for these molecules has this phenyl ring clearly out of the plane with respect to the aryleneethynylene-indole unit. It is worth noting the larger steric effect of this N-hexyl group (R^2) on the dihedral angle compared to the electronic effect of the aryl substituent R^1 group.

3.2.2. Dipole moment

The electronic nature of substituents R^3 and R^1 on the aryl rings is important in what concerns to the dipole moment μ of the molecule, (Table 1). Structural fragments in molecules **1a-i** behave electronically different: phenyleneethynylenes act as electron withdrawing (A), indole is an electron donor (D) and the phenyl group can either be a weak electron donor or electron acceptor, depending on the electronic nature of the substituent functional groups (\mathbb{R}^3 and \mathbb{R}^1). Based on this assumption, compound **1h** ($\mathbb{R}^3 = \text{OCH}_3$, $\mathbb{R}^1 = \text{CN}$) has an alternated electronic configuration D-A-D-A with a high dipole moment, while its isomeric compound **1i** ($\mathbb{R}^3 = \text{CN}$, $\mathbb{R}^1 = \text{OCH}_3$) displays an electronic configuration A-A-D-D that aligns the electronic push-pull effects in only one direction, consequently this compound has the highest dipole moment in this series. On the other side, **1a** and **1b** have intermediate dipole moment values as the substituents \mathbb{R}^1 and \mathbb{R}^3 do not have a significant electronic effect and thus the push-pull effect is derived only from the two main systems, i.e. aryleneethynylene and aryl-indole. In general, compounds with high electron donor character



Fig. 1. DFT optimized geometry at ground state for equilibrium conformer of 1a.

delocalization is practically divided in two blocks: the electronic the HOMO is distributed density of along the methoxyphenyleneethynylene-indole segment, indicating the high electron donor character of this segment. On the other hand, the LUMO is more localized on the cyanophenyl, due to the electron withdrawing nature of the CN group. Distribution of frontier orbitals in the isomeric compound **1i** is reversed: the HOMO is distributed along the indol-ethynylene segment, while the LUMO covers the cyano phenyleneethynylene fragment. All of the HOMO and LUMO calculated values are collected in Table 1, from which it can be observed that their values increase (i.e. they are less negative) as the electron donor character of the molecule increases. According to these values, the best electron donor compound of the series is **1e**, while **1d** is the best electron acceptor compound. Compounds **1h** and **1i** present intermediate value for both HOMO and LUMO values, which is in agreement with their more structured push-pull character. The band gap (Eg) was calculated as the $\Delta E_{\text{HOMO-LUMO}}$ and the lowest value corresponds to compound **1d**,

Table 1

Dihedral angles between planes I and II (α) and between II and III (β), dipole moment μ , high occupied molecular and lowest unoccupied molecular orbitals (HOMO_{th}, LUMO_{th}), optical band gap (E_{g,th}), TDDFT calculated absorption maximum ($\lambda_{abs,th}$) and oscillator strength *f* of compounds **1a-i**.

| Compound | α[°] | β[°] | μ [D] | HOMO _{th} [eV] | LUMO _{th} [eV] | $E_{g,th} [eV]$ | $\lambda_{abs,th} [nm]$ | f |
|----------|-------|-------|-------|-------------------------|-------------------------|-----------------|-------------------------|--------|
| 1a | 0.48 | 51.57 | 3.03 | -5.02 | -1.22 | 3.80 | 343 | 1.5201 |
| 1b | 1.20 | 51.48 | 3.17 | -4.91 | -1.13 | 3.78 | 342 | 1.7081 |
| 1c | 0.46 | 49.23 | 2.43 | -5.62 | -2.21 | 3.41 | 383 | 1.6264 |
| 1d | -0.32 | 48.90 | 2.58 | -5.75 | -2.78 | 2.97 | 454 | 0.9652 |
| 1e | 1.52 | 53.00 | 5.08 | -4.76 | -0.97 | 3.79 | 344 | 1.8319 |
| 1f | 0.83 | 27.33 | 1.55 | -5.57 | -2.36 | 3.21 | 405 | 1.8329 |
| 1g | 2.61 | 27.26 | 4.87 | -5.43 | -2.15 | 3.28 | 398 | 1.8487 |
| 1h | 1.90 | 48.41 | 5.56 | -5.10 | -1.82 | 3.28 | 407 | 0.9696 |
| 1i | 0.54 | 52.33 | 9.85 | -5.22 | -1.82 | 3.40 | 386 | 1.3838 |

such as **1e** ($\mathbb{R}^3 = \mathbb{R}^1 = OCH_3$), have a larger dipole moment than those with substituents with a negligible electronic contribution such as **1a** and **1b**; in contrast, compounds **1c**, **1d**, **1f** with $\mathbb{R}^3 = \mathbb{R}^1$ groups with electron attractor character have the lowest dipole moment. An intriguing case is the large difference of dipole moment between the structurally related methylketone **1f** (1.55) and aldehyde **1g** (4.87). An important observation is that the direction of the dipole moment vector changed within the series. For compounds **1a**, **1b**, **1e** and **1g**, with intermediate values of μ , the vector is directed towards the indole, as shown in Fig. 2. For compounds **1c**, **1d**, and **1f** with rather low values of μ , the vector is directed towards the aryleneethynylene. Finally, for compounds **1h** and **1i** with high values of μ , the vector is oriented towards the electron acceptor cyano group, where the negative side of the dipole of the molecule is located.

3.2.3. Molecular orbitals

The frontier (HOMO and LUMO) and subsequent molecular orbitals (HOMO-1 and LUMO+1) were calculated for all compounds studied in this work by DFT methods. In general, the HOMO-LUMO electronic distribution is clearly modified by the push-pull effects of the aryl substituent R^3 and R^1 in this series. The HOMO is mainly centered on the indole-ethynylene segment. On the contrary, the LUMOs are delocalized over the entire molecule, with a tendency to center on the electron withdrawing groups. Three particular cases: **1d**, **1h** and **1i** worth to be visualized are shown in Fig. 3. Thus, for **1d**, the LUMO is more localized on the nitrophenyl rather than on the nitrophenyleneethynylene. The isomeric compounds **1h** and **1i**, with strong electron donor and electron withdrawing groups swapped at the extremities, show a particularly pronounced change in HOMO-LUMO distribution. Thus, for **1h** the electronic

positioning these molecules as potential semiconducting materials.

3.2.4. Excitation energies

The first six excitation energies were calculated at the TTDFT/ B3LYP/6-31G* level and the simulated UV–Vis spectra were constructed with Spartan using Gaussian convolution with half height band width (HHBW) of 30 nm (see Supporting material). All compounds show a main electronic transition in the UV-blue region, with absorption maximum ($\lambda_{abs,th}$, Table 1) ranging in opposite trend to the *Eg*, i.e. the compound with the lowest *Eg* **1d** corresponds to the absorption at the longest wavelength. According to the TDDFT formalism, this band that corresponds to the first excited state is due to the HOMO→LUMO electronic transition. Other bands in the higher energy region, around 270–320 nm, were also found and they are due to the contribution of different electronic transitions. More detailed, specific data for these higher energy bands can be found in the Supporting information.

3.3. Photophysical properties

The indole and aryleneethynylene chromophore fragments of compounds **1a-i** were expected to play a role in their photophysics. Indole has been extensively studied due to its chemical similarity to tryptophan. The photophysics of indole derivatives is complex [21]; two overlapping π - π * electronic transitions ¹L_a and ¹L_b (also known as S₁ and S₁') [22–24] are responsible for their observed behavior. Experimental evidence suggests that the ¹L_b (S₁) transition has a dipole moment similar to the ground state, requires lower energy and hence, occurs first. The ¹L_a (S₁') transition requires more energy to occur, has a dipole moment larger than the ground state and consequently is sensitive to solvent polarity [25]. Although it is rare



Fig. 2. Calculated dipole moment vectors (represented by yellow arrows) obtained from the DFT optimized geometries of selected molecules. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



Fig. 3. DFT simulated frontier molecular orbitals, spatial distribution and energy levels for representative compounds 1d, 1h and 1i.

to observe both transitions separated in the same UV spectrum there are a few cases, for example with 5- or 6-hydroxyindole [21], in which this has been possible. Among different indole derivatives, 2-phenyl indoles are fluorescent molecules with quantum yields larger than 0.8 [12]. On the other hand, phenyeleneethynylenes (PEs) are fluorophores which display medium-high quantum yields in solution [13,14] and usually have only one emitting state due to a π - π * electronic transition. This localized excited state makes the maximum emission wavelength independent of the solvent. As found in the theoretical calculations, Fig. 1, the indole and the phenyleneethynylene are practically coplanar in the ground state with an extended electronic delocalization.

When absorption of compounds 1a-i was studied in toluene, dichloromethane and DMSO the absorption coefficient was high and no significant changes in the wavelength maxima were observed. For these compounds the main peak in the UV spectra (λ_{abs}) is located between 330 nm and 406 nm, depending on the overall conjugation of the molecule that in turn is modulated by the substituents on the aryl groups. (Tables 2-4). There is a good agreement between the experimental and simulated spectra and between the absorption maxima collected in Table 1 (theoretical) and 2 (experimental), theoretical values are slightly larger than experimental ones as usually found when TDDFT simulation is carried out. [26,27] On the other hand, pronounced changes in the emission spectra of these compounds due to change in solvent polarity were observed (Tables 2–4). For example, while compound 1c showed nearly identical UV absorption spectra in all solvents $(\lambda_{abs} 363 \text{ nm in toluene}, 367 \text{ nm in dichloromethane and 360 nm in})$ DMSO, see entry 3 in Tables 2-4), its emission spectra showed a bathochromic shift with the polarity of the solvent (λ_{em} 416, 431 nm in toluene, 426 nm in dichloromethane and 460 nm in DMSO). This solvatofluorochromism is in line with reported observations in indole derivatives [21–24,28]. It is worth mentioning that solvent dependent spectral shifts of dyes are ordinarily studied by applying the Lippert-Mataga equation [29,30]. This equation describes the Stokes shifts as a function of the change in the dipole moment of the dye upon excitation. Plots of the Stokes shift vs. the polarizability function of several solvents are drawn, and the slope of the fitted lines can give the difference between the ground and excited state dipole moment $\Delta \mu_{eg}$. When the ground state dipole moment is known or calculated (as in our case), the excited state dipole moment can be derived. In this paper, we used DCM, DMSO and toluene as they are good solvents for the entire family, allowing a quantitative and overall picture of the photophysical properties of the molecules. Several solvents of different polarity, normally 10 to 20, are needed to build those plots. However, some of them such as alkanes and alcohols do not dissolve any of the molecules studied in this work, others such as THF and acetonitrile dissolve, at least partially, some molecules but not all of them. Based on these limitations, the determination of the excited state dipole moment could not be realized at this time by Lippert-Mataga plots but will be considered for some selected molecules in future work. Whereas no general feature can describe the emission behavior of the whole series, there are some interesting observations: i) **1a**, **1b** show excitonic like spectra and no significant solvatochromism as the differences in the emission maxima and quantum yields are within the experimental error of the determination, ii) the spectra of **1c**, **1e**, **1f**, **1g**, **1h** and **1i**, which are excitonic in toluene, become broader in dichloromethane and even more in DMSO. For example, the HHBW of **1f** increases from 49 nm in toluene to 79 nm in CH₂Cl₂ and to 89 nm in DMSO, accordingly, the Stokes shift also increases, iv) for all these molecules, the quantum yield decreases with the polarity of the solvent.

The Stokes shift values (Δv) in toluene are in the range of molecules that undergo geometry change after excitation [26,27], but in general lower to those usually reported for ICT states [31]. Intramolecular charge transfer can eventually occur in DMSO, and in particular for **1h** and **1i**, which is in agreement with their observed large HHBW and Stokes shift and can explain their lower fluorescence quantum yields found in this solvent.

A particular case is compound **1d**, for which the fluorescence spectrum strongly red shifts and decreases in intensity with increasing excitation wavelength (Fig. 4). Contrary to what was observed for the rest of the compounds, the excitation spectrum of 1d does not show the electronic transition that gives rise to the absorption band at 403 nm. This result could be explained on the basis that a non-emissive state is reached after excitation, perhaps related to the nitrophenyl chromophore which by coincidence appears at the same wavelength (400–405 nm). There is overlap between the absorption and emission spectra and then we cannot discard that the fluorescence bands are derived from internal charge transfer. This interpretation could explain why the emission band shifts and the large Stokes shift; the shift of the emission band in a very polar solvent (DMSO) and the low quantum yield found. As pointed out previously, indoles present two excited states S1 and S1', which according to the recent model by Catalán [24] the lower energy excited state S₁' is highly dipolar giving a structureless emission that shifts depending of the polarity of the medium. However, the theoretical study of the molecules in this work already mentioned, suggested that conjugation involves both the indole and phenyleethynylene moieties, i.e. the indole group is not acting as an isolated chromophore and in consequence we do not relate entirely the behavior of these molecules to the S1' properties of the pure indole chromophore.

Besides **1d**, all of the other molecules had very high fluorescence quantum yields (φ) with monoexpontential time decay and lifetimes between 1 and 2 ns? Notably, the measured quantum yield (φ) for **1a**, **1 b** and **1c** (in toluene) **1a**, **1e** (in dichloromethane) and **1b** (in DMSO) gave a value larger than 1, which for definition must be \leq 1. It is important to specify that the fluorescence quantum yield was determined by the indirect dilution method of Williams [15] using quinine sulfate as standard and full precautions were

| Table 2 | |
|---|----------|
| Optical properties of compounds 1a-i in | toluene. |

| Compound | Eg _{opt} [eV] | $\lambda_{abs} [nm]$ | $\epsilon [10^4 M^{-1} cm^{-1}]$ | λ _{em} [nm] | HHBW _{em} [nm] | $\Delta v [cm^{-1}]$ | Φ [%] ^a | τ [ns] | $k_{rad} \left[s^{-1} \right]$ |
|----------|------------------------|----------------------|------------------------------------|----------------------|-------------------------|-----------------------|-------------------------|--------|---------------------------------|
| 1a | 3.31 | 330 | 3.4 | 382, 399 | 56 | 4125 | 108.0 | 1.21 | $8.92 \cdot 10^{8}$ |
| 1b | 3.29 | 333 | 3.5 | 385, 403 | 56 | 4056 | 124.5 | 1.14 | $1.09 \cdot 10^9$ |
| 1c | 3.04 | 363 | 4.6 | 416, 431 | 55 | 3510 | 123.0 | 1.34 | $0.92 \cdot 10^{9}$ |
| 1d | 2.69 | 397 | 3.9 | 495 | 75 | 4987 | 15.7 | 1.51 | $0.10 \cdot 10^9$ |
| 1e | 3.27 | 333 | 4.3 | 384, 402 | 56 | 3989 | 101.9 | 1.14 | $0.89 \cdot 10^9$ |
| 1f | 2.94 | 382 | 4.7 | 419, 440 | 49 | 2312 | 91.2 | 1.10 | $0.83 \cdot 10^9$ |
| 1g | 2.89 | 385 | 2.5 | 427, 450 | 53 | 2555 | 76.3 | 1.12 | $0.68 \cdot 10^9$ |
| 1h | 2.98 | 360 | 3.6 | 422 | 63 | 4081 | 60.0 | 1.51 | $0.39 \cdot 10^9$ |
| 1i | 2.99 | 357 | 2.0 | 417, 435 | 45 | 4030 | 43.7 | 1.18 | $0.37 \cdot 10^9$ |

^a The quantum yield has an accuracy of $\pm 10\%$ of the value shown.

| Table 3 | |
|---------------------------------|---|
| Optical properties of compounds | 1a-i in CH ₂ Cl ₂ . |

| Compound | Eg _{opt} [eV] | λ_{abs} [nm] | $\epsilon \ [10^4 \ M^{-1} cm^{-1}]$ | λ _{em} [nm] | HHBW _{em} [nm] | $\Delta \nu [cm^{-1}]$ | Φ [%] ^a | τ, [ns] | $k_{rad} \left[s^{-1} \right]$ |
|----------|------------------------|----------------------|--------------------------------------|----------------------|-------------------------|-------------------------|-------------------------|---------|---------------------------------|
| 1a | 3.33 | 332 | 3.8 | 387, 399 | 59 | 4281 | 120.0 | 1.35 | 8.88 · 10 ⁸ |
| 1b | 3.28 | 333 | 3.9 | 387, 400 | 59 | 4190 | 94.0 | 1.23 | $7.64 \cdot 10^{8}$ |
| 1c | 2.98 | 367 | 5.0 | 426 | 62 | 3774 | 99.2 | 1.43 | $6.94 \cdot 10^{8}$ |
| 1d | 2.58 | 403 | 4.0 | 456 | 64 | 2884 | 0.2 | 0.42 | $4.76 \cdot 10^{6}$ |
| 1e | 3.27 | 335 | 4.5 | 386 | 59 | 3944 | 114.4 | 1.18 | $9.69 \cdot 10^{8}$ |
| 1f | 2.92 | 381 | 5.1 | 449 | 79 | 3975 | 77.2 | 1.47 | $5.25 \cdot 10^{8}$ |
| 1g | 2.86 | 390 | 2.8 | 460 | 76 | 3902 | 62.7 | 1.66 | $3.78 \cdot 10^{8}$ |
| 1h | 2.99 | 364 | 3.7 | 463 | 79 | 5874 | 100.0 | 2.08 | $4.81 \cdot 10^{8}$ |
| 1i | 3.04 | 353 | 2.1 | 444 | 67 | 5806 | 100.7 | 2.06 | $4.89 \cdot 10^{8}$ |

^a ±10% of error.

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 Table 4

 Optical properties of compounds 1a-i in DMSO.

| Compound | Eg _{opt} [eV] | λ_{abs} [nm] | $\epsilon \ [10^4 \ M^{-1} cm^{-1}]$ | λ _{em} [nm] | HHBW _{em} [nm] | $\Delta v [cm^{-1}]$ | Φ [%] ^a | τ [ns] | $k_{rad} \left[s^{-1} \right]$ |
|----------|------------------------|----------------------|--------------------------------------|----------------------|-------------------------|----------------------|-------------------------|--------|---------------------------------|
| 1a | 3.27 | 333 | 3.5 | 403 | 58 | 5216 | 89.5 | 1.36 | 0.66 · 10 ⁹ |
| 1b | 3.23 | 335 | 3.8 | 405 | 58 | 5159 | 111.6 | 1.23 | $0.91 \cdot 10^{9}$ |
| 1c | 2.88 | 360 | 4.1 | 460 | 82 | 6039 | 43.4 | 1.92 | $0.23 \cdot 10^9$ |
| 1d | 2.51 | 406 | 3.5 | 458 | 73 | 2766 | $2.8 \cdot 10^{-2}$ | 0.17 | $1.64 \cdot 10^{6}$ |
| 1e | 3.22 | 337 | 4.6 | 410 | 58 | 5283 | 56.9 | 1.23 | $0.46 \cdot 10^9$ |
| 1f | 2.76 | 386 | 4.7 | 493 | 89 | 5623 | 12.7 | 1.40 | $0.91 \cdot 10^{8}$ |
| 1g | 2.71 | 395 | 2.6 | 506 | 86 | 5554 | 4.4 | 0.58 | $0.76 \cdot 10^{8}$ |
| 1h | 2.87 | 367 | 3.1 | 499 | 86 | 7208 | 64.8 | 2.32 | $0.28 \cdot 10^9$ |
| 1i | 2.93 | 353 | 1.8 | 451 | 69 | 6156 | 40.0 | 2.22 | 0.18 · 10 ⁹ |

^a $\pm 10\%$ of error.



Fig. 4. Fluorescence spectrum of **1d** in toluene obtained at 320 (red solid line), 360 (black dash line) and 400 nm (black dotted line) of excitation wavelength. The inserted figure corresponding to excitation spectra, including **1a** (green circles), was added as reference. *Indicates the peak related to the emission scattering. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

taken to avoid experimental artifacts (see Supporting information). However, it is possible that these excessive φ values arise from other sources; it may be that the absorption and emission bands used to calculate the quantum yield do not entirely correspond to the same process, since the excited state ${}^{1}L_{b}$ gives rise to ${}^{1}L_{a}$ and the observed emission may have components from both states, this has been called an anomalous emission [21]. In addition, other simultaneous emission processes can also occur. For example, by means of ultrafast electron diffraction studies on indole, Zewail has proposed the existence of triplet states. These triplets by means of intersystem crossing [32] can repopulate the first excited state [33,34]. This process can occur by two mechanisms: thermally activated delayed fluorescence (TADF, in which a small energy gap between singlet and triplet states allows reversible intersystem crossing and thermal repopulation of S state from T state) and triplet-triplet annihilation (which consists of the combination of two triplets to form a singlet state from which emission is observed). Very high quantum yields and quite small Stokes shifts attributed to thermally activated delayed fluorescence (TADF) have been reported [34]. The critical point to achieve TADF is the combination of a small energy gap between singlet and triplet excited states and a radiative decay constant (k_{rad}) larger than 10^6 s⁻¹; according to our data, the observed $k_{rad} \sim 10^7 \, s^{-1}$ in our compounds satisfies this requirement. However, at present time there is no experimental evidence to unambiguously support (or rule out) any of these possible pathways. The observation that the measured value of φ for this series is generally lower in DMSO is likely due to charge transfer, which is also indicated by the larger Stokes shifts observed in this solvent, this makes possible non-radiative deactivation pathways. However, not only the solvent polarity plays an active role on the deactivation process, structural factors are important as well [22–24]. For example, contrary to all other congeners, compound **1b** shows high quantum yield in the three solvents tested despite their different polarity.

3.4. Electrochemical studies

Cyclic voltammetry. Table 5 summarizes the electrochemical parameters of all of the molecules, which exhibit the following behavior: a) when oxidation or reduction (if any) processes are separately analyzed, both are irreversible in most of the cases; b) products are electroactive only when forward (from +3 to -3 V) scans are analyzed, with the exception of **1c, 1d** and **1f** whose voltammograms could be obtained in either direction (from +3 to -3 V or by reverse scan from -3 V to +3 V); c) all of the other compounds tend to deposit on the electrodes during the oxidation

process. These deposits explain the high current peak intensity observed in the voltammograms and suggests that transport by adsorption is the dominant process, Fig. 7S.

In order to better understand the electrochemical behavior of these compounds, Fig. 5 shows the voltammograms for 1h, representative of the whole series, along with a phenyleneethynylene trimer (**3PEBz**) and the 5-bromo-2-methylindole (**BMI**), used for comparison as references to the electrochemical behavior of the ethynylene and indole fragments contained in the indoles 1a-i reported herein. Thus, it is observed that the phenyleneethynylene is either difficult to be oxidized (+1.78 V) or reduced (-2.09 V) [35]. On the contrary, the first oxidation (+1.13 V) and reduction (-1.04 V) peaks of the 5-bromo-2-methyl indole (BMI) indicate that these processes are more likely to occur, but still they are irreversible. It has been reported that upon anodic electro oxidation indoles form soluble or insoluble products depending on the electron donor/acceptor ability of the substituting group on the indole [36]. Furthermore, it is known that polymerization of indoles can occur at the C-2 and C-3 positions [37,38]. Thus, 5-bromo-2methylindole (BMI), used as reference in this work, underwent electro oxidation evidenced by appearance of a light green color in solution and a green-black solid deposit on both the GC and platinum wire electrodes; in addition, the anodic peaks were very broad. In contrast, only one peak was observed in the first cathodic cycle at -1.04 V. This peak was shifted to more negative values at -1.67 V for subsequent cycles, likely due to electrochemical modification of the structure. From these data and Fig. 5 it is clear that the most energetically favorable oxidation and reduction occurs in the indole fragment, while these processes require substantially more energy to occur in the acetylene group. Accordingly, the first anodic and cathodic peaks in all of the compounds **1a-i** on this series were assigned to the oxidation-reduction of the indole group and their values were used to calculate their HOMO and LUMO energies. Variations in the magnitude of these energies are a consequence of the electronic push/pull effects of the functional groups at the extremities. It is worth mentioning that the expected aryleneethynylene reduction band was only observable for compounds 1a, 1d, 1f, 1g, and 1h, substituted with strong electron withdrawing groups. The formation of insoluble films deposited on the working electrode during electro oxidation indicates electrochemical modification of indoles **1a-i**. According to literature [39] the presence of two or more peaks in the voltamogramms of conjugated macromolecules can be due to the formation of polarons (lower voltage oxidation peaks) and bipolarons (oxidation peaks at higher voltages) or to the separate contribution of the different functional groups on the molecule [37,40] For example, in isomeric compounds **1h** and **1i**, it may be considered that the first group to be electrooxidized is the indole (peak + I, in curve (b) in Fig. 5), followed by the electron donor OCH_3 (peak + II) and, at last, the



Fig. 5. Comparative electrochemical oxidative and reductive potential of a) 5-bromo-2-methylindole (MBI), b) 1h and c) phenyleneethynylene (3PEBz).

phenyleneethynylene group (peak + III).

4. Conclusion

In summary, novel 2-aryl, 6-(aryleneethynylene)-1*H*-indoles were readily prepared by one pot Sonogashira coupling and

Table 5

Electrochemical properties of compounds **1a-i** studied in this work and 5-bromo-2-methylindole (**BMI**) and a phenyleneethynylene trimer (**3PEBz**) used as reference; V vs. Ag/ AgCl.

| Compound | $E_{red}^{II}(V)$ | $E_{red}^{I}(V)$ | $E_{ox}^{I}(V)$ | $E_{ox}^{II}(V)$ | $E_{ox}^{III}(V)$ | HOMO (eV) | LUMO (eV) | Eg (eV) |
|----------|-------------------|------------------|-----------------|------------------|-------------------|-----------|-----------|---------|
| 1a | _ | -1.07 | +1.07 | +1.42 | +2.37 | -5.87 | -3.73 | 2.14 |
| 1b | _ | -0.99 | +1.07 | +1.48 | +2.25 | -5.87 | -3.81 | 2.06 |
| 1c | -2.23 | -1.01 | +1.32 | +1.70 | +2.26 | -6.12 | -3.79 | 2.33 |
| 1d | -1.64 | -1.11 | +1.31 | +1.70 | +2.38 | -6.11 | -3.69 | 2.42 |
| 1e | _ | -1.09 | +0.89 | +1.66 | +2.26 | -5.69 | -3.71 | 1.98 |
| 1f | -1.93 | -1.02 | +1.04 | +1.60 | +2.52 | -5.84 | -3.78 | 2.06 |
| 1g | -1.98 | -1.04 | +1.07 | +1.52 | +1.99 | -5.87 | -3.76 | 2.11 |
| 1h | -2.14 | -0.99 | +0.96 | _ | +2.45 | -5.76 | -3.81 | 1.95 |
| 1i | _ | -1.09 | +1.19 | +1.52 | +2.17 | -5.99 | -3.71 | 2.28 |
| BMI | _ | -1.04 | +1.13 | +1.61 | - | -5.93 | -3.76 | 2.17 |
| 3PEBz | _ | -2.09 | +1.78 | _ | _ | -6.58 | -2.71 | 3.87 |

fluoride promoted cyclization. N-alkylation of these molecules gave very soluble molecules in common organic solvents. The linking of two known fluorophores, the 4-substituted phenyleneethynylene and the 2-arylindole has given new compounds with intense fluorescence in which the substituent groups on the aryls modulate the electronic density, molecular orbitals, band gap and dipole moments of these molecules. These compounds exhibit absorption and excitation in the UV, which are independent of the solvent. On the contrary, depending on the polarity of the solvent used (toluene, dichloromethane and DMSO) a strong solvatochromism was observed. These compounds display intense fluorescence and large Stokes shifts; it is possible that delayed fluorescence is at play and this could account for the observed quantum yields larger than 1. Cyclic voltammetry studies indicate that the electrochemical redox processes are irreversible and DFT calculations indicate that they are centered on the indole fragment. We believe that the synthesis and initial study of the photophysical properties of these new indole derivatives will be helpful for the design of new molecules with improved properties.

Acknowledgements

MFJ is thankful to CONACyT for a graduate fellowship, authors are also thankful to CONACYT for funding this research (grant CB-2013-221360).

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.dyepig.2016.05.017.

References

- Muthuraj B, Layek S, Balaji SN, Trivedi V, Iyer PK. Multiple function fluorescein probe performs metal chelation, disaggregation, and modulation of aggregated aβ and Aβ-Cu complex. Chem Neurosci 2015;6:1880–91. DOI: 0.1021/ acschemneuro.5b00205.
- [2] Fan Li, Gao S-Q, Li Z-B, Niu W-F, Zhang W-J, Shuang S-M, et al. An indolecarbazole-based ratiometric emission pH fluorescent probe for imaging extreme acidity. Sens Actuators B 2015;221:1069–76. http://dx.doi.org/ 10.1016/j.snb.2015.07.076.
- [3] Xu W, Kim T-H, Zhai D, Ar JC, Zhang L, Kale AA, et al. Make caffeine visible: a fluorescent caffeine "Traffic light" detector. Sci Rep 2013;3:2255. http:// dx.doi.org/10.1038/srep02255.
- [4] Jeyanthi D, Iniya M, Krishnaveni K, Chellappa D. Novel indole based dual responsive "turn-on" chemosensor for fluoride ion detection. Spectrochim Acta Part A 2015;136:1269-74. http://dx.doi.org/10.1016/j.saa.2014.10.013.
- [5] Guo L, Chan MS, Xu D, Tam DY, Bolze F, Lo PK, et al. Indole-based cyanine as a nuclear RNA-selective two-photon fluorescent probe for live cell imaging. ACS Chem Biol 2015;10:1171–5. http://dx.doi.org/10.1021/cb500927r.
- [6] Cheng L, He W, Gong H, Wang C, Chen Q, Cheng Z, et al. PEGylated micelle nanoparticles encapsulating a non-fluorescent near-infrared organic dye as a safe and highly-effective photothermal agent for in vivo cancer therapy. Adv Funct Mater 2013;23:5893–902. http://dx.doi.org/10.1002/adfm.201301045.
- [7] Li M, Teh C, Ang CY, Tan SY, Luo Z, Qu Q, et al. Near-infrared light-absorptive stealth liposomes for localized photothermal ablation of tumors combined with chemotherapy. Adv Funct Mater 2015;25:5602–10. http://dx.doi.org/ 10.1002/adfm.201502469.
- [8] Setaro A, Bluemel P, Chandan M, Hecht S, Reich S. Non-covalent functionalization of individual nanotubes with spiropyran-based molecular switches. Adv Funct Mater 2012;22:2425–31. http://dx.doi.org/10.1002/ adfm.201102451.
- [9] Li H, Pang M, Wu B, Meng J. Synthesis, crystal structure and photochromism of a novel spiro[indoline-naphthaline]oxazine derivative. J Mol Struct 2015;1087:73–9. http://dx.doi.org/10.1016/j.molstruc.2015.01.050.
- [10] Li Q, Zou J, Chen J, Liu Z, Qin J, Li Z, et al. New indole-based light-emitting oligomers: structural modification, photophysical behavior, and electroluminescent properties. J Phys Chem B 2009;113:5816–22. http://dx.doi.org/ 10.1021/jp9005372.
- [11] Ojala A, Petersen A, Fuchs A, Lovrincic R, Pölking C, Trollmann J, et al. Merocyanine/C60 planar heterojunction solar cells: effect of dye orientation on exciton dissociation and solar cell performance. Adv Funct Mater 2012;22: 86–96. http://dx.doi.org/10.1002/adfm.201101697.
- [12] Berlman IB, editor. Handbook of fluorescence spectra of aromatic molecules. second ed. New York: Acad. Press Inc; 1971.

- Bunz UHF. Poly(aryleneethynylene)s: syntheses, properties, structures and applications. Chem Rev 2000;100:1605–44. http://dx.doi.org/10.1021/ cr990257j.
- [14] Moggio I, Arias E. Biomimetic and supramolecular systems research. In: Lima AH, editor. Chapter viii, molecular engineering of phenyleneethynylenes: towards specific molecular and supramolecular organization for optoelectronics. New York: Nova Science Publishers, Inc.; 2008, p. 179.
- [15] Williams ATR, Winfield SA, Miller JN. Relative fluorescence quantum yields using a computer controlled luminescence spectrometer. Analyst 1983;108: 1067–71. http://dx.doi.org/10.1039/AN9830801067.
- [16] El-Daly SA, El-Azim SA, Elmekawey FM, Elbaradei BY, Shama SA, Asiri AM. Photophysical parameters, excitation energy transfer and photoreactivity of 1,4-Bis(5-phenyl-2-oxazolyl)benzene (POPOP) laser dye. Int J Photoenergy 2012;2012:10. http://dx.doi.org/10.1155/2012/458126. Article ID 458126.
- [17] Al-Ibrahim M, Roth H-K, Schroedner M, Konkin A, Zhokhavets U, Gosbsch G, et al. The influence of the optoelectronic properties of poly(3alkylthiophenes) on the device parameters in flexible polymer solar cells. Org Elec 2005;6:65-7. http://dx.doi.org/10.1016/j.orgel.2005.02.004.
- [18] Liu Y, Liu MS, Jen AK-Y. Synthesis and characterization of a novel and highly efficient light-emitting polymer. Acta Polym 1999;50:105. http://dx.doi.org/ 10.1002/(SICI)1521-4044(19990201)50:2/3<105::AID-APOL105>3.0.CO;2-0.
- [19] Valois-Escamilla I, Alvarez-Hernandez A, Rangel-Ramos LF, Suarez-Castillo OR, Ayala-Mata F, Zepeda-Vallejo G. Synthesis of 6-bromo-2-arylindoles using 2iodobenzoic acid as precursor. Tetrahedron Lett 2011;52:3726-8. http:// dx.doi.org/10.1016/j.tetlet.2011.05.040.
- [20] Gelman D, Buchwald SL. Efficient palladium-catalyzed coupling of aryl chlorides and tosylates with terminal alkynes: use of a copper cocatalyst inhibits the reaction. Angew Chem Int 2003;42:5993–6. http://dx.doi.org/10.1002/ anie.200353015.
- [21] Meng X, Harricharran T, Juszczak LJ. A spectroscopic survey of substituted indoles reveals consequences of a stabilized ¹L_b transition. Photochem Photobiol 2013;89:40–50. http://dx.doi.org/10.1111/j.1751-1097.2012.01219.x.
- [22] Catalán J, Catalán JP. Questioning the photophysical model for the indole chromophore in the light of evidence obtained by controlling the non-specific effect of the medium with 1-chlorobutane as solvent. Phys Chem Chem Phys 2011;13:15022–30. http://dx.doi.org/10.1039/c1cp21380f.
- [23] Catalán J. Fluorosolvatochromism of monomethyl indoles: further evidence in support of a new photophysical model for the indole chromophore. J Phys Org Chem 2015;28:329–36. http://dx.doi.org/10.1002/poc.3414.
- [24] Catalán J. The first UV absorption band for indole is not due to two simultaneous orthogonal electronic transitions differing in dipole moment. Phys Chem Chem Phys 2015;17:12515–20. http://dx.doi.org/10.1039/c5cp01170a.
- [25] Eftink MR, Selvidge LA, Callis PR, Rehms AA. Photophysics of indole derivatives: experimental resolution of La and Lb transitions and comparison with theory. J Phys Chem 1990;94:3469-79. http://dx.doi.org/10.1021/ j100372a022.
- [26] James PV, Sudeep PK, Suresh CH, Thomas KG. Photophysical and theoretical investigations of oligo(p-phenyleneethynylene)s: effect of alkoxy substitution and alkyne-aryl bond rotations. J Phys Chem A 2006;110:4329–37. http:// dx.doi.org/10.1021/jp0551840.
- [27] Castruita G, García V, Arias E, Moggio I, Ziolo R, Ponce A, et al. Synthesis, optical and structural properties of sanidic liquid crystal (cholesteryl)benzoate-ethynylene oligomers and polymer. J Mater Chem 2012;22:3770–80. http://dx.doi.org/10.1039/C2JM14918D.
- [28] Eisinger J, Navon G. Fluorescence quenching and isotope effect of tryptophan. J Chem Phys 1969;50:2069-77. http://dx.doi.org/10.1063/1.1671335.
- [29] Lippert E. Dipolmoment und elektronenstruktur von angeregten molekülen. Z Naturforsch A Phys Sci 1955;10:541–5.
- (a) Mataga N, Kaifu Y, Koizumi M. The solvent effect on fluorescence spectrum change of solute-solvent interaction during the lifetime of excited solute molecule. Bull Chem Soc Jpn 1955;28:690–1.
 (b) Mataga N, Kaifu Y, Koizumi M. Solvent effects upon fluorescence spectra and the dipole moments of excited molecules. Bull Chem Soc Jpn 1956;29: 465–70.
- [31] Wakamiya A, Mori K, Yamaguchi S. 3-Boryl-2,2'-bithiophene as a versatile core skeleton for full-color highly emissive organic solids. Angew Chem Int Ed 2007;46:4273-6. http://dx.doi.org/10.1002/anie.200604935.
- [32] Park ST, Gahlmann YH, Feenstra JS, Zewail AH. Ultrafast electron diffraction reveals dark structures of the biological chromophore indole. Angew Chem Int Ed 2008;47:9496–9. http://dx.doi.org/10.1002/anie.200804152.
- [33] Endo A, Sato K, Yoshimura K, Kai T, Kawada A, Miyazaki H, et al. Efficient upconversion of triplet excitons into a singlet state and its application for organic light emitting diodes. App Phys Lett 2011;98:083302. DOI: 10.1063-1.3558906.
- [34] Uoyama H, Goushi K, Shizu K, Nomura H, Adachi C. Highly efficient organic light-emitting diodes from delayed fluorescence. Nature 2012;492:234–40. DOI: 10.1038-nature11687.
- [35] Wilson JN, Windscheif PM, Evans U, Myrick ML, Bunz UHF. Band gap engineering of poly(p-phenyleneethynylene)s: cross-conjugated PPE–PPV hybrids. Macromolecules 2002;35:8681–3. http://dx.doi.org/10.1021/ ma025616i.
- [36] Waltman RJ, Diaz AF, Bargon J. Substituent effects in the electropolymerization of aromatic heterocyclic compounds. J Phys Chem 1984;88: 4343–6. http://dx.doi.org/10.1021/j150663a030.
- [37] Zotti G, Zecchin S, Schiavon G, Seraglia R, Berlin A, Canavesi A. Structure of

polyindoles from anodic coupling of indoles: an electrochemical approach. Chem Mater 1994;6:1742–8. http://dx.doi.org/10.1021/cm00046a029.

- [38] Talbia H, Monardb G, Loosb M, Billauda DJ. Theoretical study of indole polymerization. J Mol Struct 1998;434:129–34. http://dx.doi.org/10.1016/S0166-1280(98)00092-X.
- [39] Winokur M, Moon YB, Heeger AJ, Barker J, Boot DC, Shirakawa H. X-ray scattering from sodium-doped polyacetylene: incommensurate-

commensurate and order-disorder transformations. Phys Rev Lett 1987;58:

2329–32. http://dx.doi.org/10.1103/PhysRevLett.58.2329.
[40] Schenning APHJ, Tsipis AC, Meskers SCJ, Beljonne D, Meijer EW, Bredas JL. Electronic structure and optical properties of mixed phenylene vinylene/ phenylene ethynylene conjugated oligomers. Chem Mater 2002;14:1362–8. http://dx.doi.org/10.1021/cm0109185.