Arylamino-fluorene derivatives: Optically induced electron transfer investigation, redox-controlled modulation of absorption and fluorescence

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GRAPHICAL ABSTRACT



Biarylaminofluorene-based systems with donor- π -donor (D- π -D) structure, with mixed-valence behavior, exhibit redox-controlled modulation of absorption and fluorescence

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3	fluorescence
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1 ABSTRACT

A series of biarylaminofluorene-based systems with donor- π -donor (D- π -D) structure have been 2 designed and synthesized in order to study the dependence on the π -conjugated bridge length of the 3 intervalence charge-transfer transitions (IV-CT) and of the electronic coupling between the redox 4 5 centers. To this purpose cyclic voltammetry, UV/Vis-NIR, fluorescence spectroscopy and 6 computational investigations have been carried out to characterize the electronic structure of the compounds in the neutral as well as in the mono- and dication states. Additionally, a study of 7 related D- π compounds has been performed to elucidate the effect of the interaction between two 8 9 redox centers. Interestingly it was observed that the mono- and dication species exhibit intense transition bands in the NIR region, in the 10000-15000 cm⁻¹ range, whose intensity depends on the 10 oxidation state and thus it can be reversibly tuned by an applied potential. In a similar way, all 11 12 compounds show an oxidation state dependent fluorescence which leads to electrofluorochromism. Particularly significant is the mixed valence behavior that provides these systems singular 13 optoelectronic properties, making them excellent active components for electrochromic and 14 electrofluorochromic applications. 15

1 GRAPHICAL ABSTRACT





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4 Biarylaminofluorene-based systems with donor- π -donor (D- π -D) structure, with mixed-valence

5 behavior, exhibit redox-controlled modulation of absorption and fluorescence

1 KEYWORDS:

- 2 Mixed-Valence, Fluorene, Triarylamines, Optically induced electron transfer, NIR-
- 3 Electrochromism, Electrofluorochromism.

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Journal Prevention

1 **1. INTRODUCTION**

Organic conjugate compounds have been widely used as active materials in many optoelectronic 2 applications, including organic dyes solar cells (DSSCs),[1-4] organic light-emitting diodes 3 4 (OLEDs),[5-7] electrochromic devices (ECDs),[8-10] and electrofluorochromic devices 5 (ECFDs),[11-14] organic field-effect transistors (OFETs)[15-19] and as fluorescent materials for 6 bioimaging applications.[20-25] Since intramolecular electron transfer processes underlie 7 optoelectronic principles, their investigation and understanding are of crucial importance to afford a 8 rational design of materials with well-defined optoelectronic characteristics. Since decades, organic 9 mixed-valence systems (MVs) have been used as model compounds for electron transfer or hole transfer investigations.[26-35] Typically, MV systems consist of two or more chemically equivalent 10 redox centers with different formal oxidation states and connected to each other by a saturated or 11 unsaturated molecular bridge.[36-42] Robin and Day in 1967[10] classified MV systems into three 12 13 classes, based on the charge distribution on the molecule and on the strength of electronic coupling 14 between the redox centers: class-I identifies a system in which the charge is localized on only one redox center and the redox centers behave as separate entities (electron coupling is zero); class-II 15 16 includes the charge-localized systems with weak electron coupling, such that just a small delocalization of charge between the redox centers occurs and a fraction of charge can be 17 18 transferred from one redox center to the other; class-III refers to systems with strong electron 19 coupling, where the charge is completely delocalized between the redox centers. A number of MV species were prepared with various π -conjugated bridges having different electronic nature and 20 21 various lengths, with the aim to investigate the strength of the electron coupling and the charge 22 delocalization in these systems.[43, 44] MV systems show unique optoelectronic transitions 23 associated with intramolecular charge transfer; in particular, the electron coupling optically induced between the redox centers gives rise to the intervalence charge transfer transition band, known as 24 25 IV-CT, that appears in the Vis or NIR region, depending on the nature of the molecular structure and on the behavior of the redox centers. Arylamine moieties are the most widely used as redox 26

centers in a number of MVs in order to investigate hole transfer processes, since they are able to
 form stable radical cations at low potential, showing excellent reversible redox processes.[33] For
 this reason, the arylamino-derivatives are very interesting as hole-transporting organic materials in
 organic light-emitting diodes[45-47] and in hybrid and all-organic solar cells.[48-51]

In our previous work, [36, 52] we have designed and synthesized interesting arylamine-based MV 5 6 compounds, belonging to class II/III, with an effective electron coupling between the redox centers, 7 which exhibit a very intense IV-CT band, well separated from other radical transition bands. Such 8 feature, together with the excellent reversibility of the redox processes, made them appealing for 9 NIR-electrochromic applications. The aforementioned materials were used as anodic components in electrochromic devices showing a great ability to switch from almost colorless to colored states, 10 including the NIR range.[53] A further interesting application field for emissive materials showing 11 a MV behavior is the electrofluorochromism; as we have demonstrated in our previous work, the 12 13 arylamine-fluorene based MV system showed excellent electrofluorochromic properties due to the stabilization of the radical ions by electron coupling between the redox centers.[13] 14

15 On the basis of these last results, in the present work we focused our interest on deepen the study on 16 biarylaminofluorene-based systems (Fig. 1), going to design and synthesize a series of MV compounds (I-III) with $D-\pi$ -D structure, based on two arylamine moieties (D) as redox centers 17 connected by π -conjugated spacers (π) of different length, based on the fluorene system. In order to 18 19 investigate the strength of the electron coupling in the resulting MV radical cations $(D-\pi-D)^+$, spacers with a different number of bonds between the redox centers have been used: fluorene for 20 21 compound **I**, phenyl-fluorene-phenyl for compound **II** and phenylethynyl-fluorene-phenylethynyl for compound III. Our focus has been to study the dependence of electronic transitions associated 22 23 with different intra-molecular charge transfer processes on the nature of the π -conjugated bridge. To better understand the role of the redox centers coupling in the different molecules, the mono-24 arylamine derivatives IV, V and VI have been also prepared as model compounds for the 25 corresponding bis-arylamino derivatives, I, II and III, respectively. So, they have been synthesized 26

1 using the same π - conjugated moiety used as spacers in the correlated bis-arylamine I, II and III. Photophysical, electrochemical and time-dependent density functional theory (TD-DFT) 2 investigations have been carried out to understand the fundamental properties of the sinthesized 3 materials. Absorption and emission spectroelectrochemistry were performed in order to disclose 4 5 their electrochromic and electrofluorochromic potentialities. In detail, here we report the synthesis 6 and characterization of bis(arylamino)- (I-III) and monoarylamino-fluorene (I-VI) derivatives: 9.9dihexyl-N2,N2,N7,N7-tetrakis(4-methoxyphenyl)-9H-fluorene-2,7-diamine (I), 4,4'-(9,9-dihexyl-7 8 9H-fluorene-2,7-diyl)bis(N,N-bis(4-methoxyphenyl)aniline) (II), 4,4'-((9,9-dihexyl-9H-fluorene-9 2,7-diyl)bis(ethyne-2,1-diyl))bis(N,N-bis(4-methoxyphenyl)aniline) (III), 9,9-dihexyl-N,N-bis(4methoxyphenyl)-9H-fluoren-2-amine 4-(9,9-dihexyl-9H-fluoren-2-yl)-N,N-bis(4-10 (**IV**), methoxyphenyl)aniline 4-((9,9-dihexyl-9H-fluoren-2-yl)ethynyl)-N,N-bis(4-11 **(V)**,

12 methoxyphenyl)aniline (VI) (Fig.1).

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Fig. 1. Molecular structures of MV compounds I, II, III, IV, V and VI.

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3 2. RESULTS AND DISCUSSION

4 2.1 Synthesis.

A straightforward synthetic strategy based on palladium-catalyzed C-N (Buchwald-Hartwig) and C-5 6 C (Suzuki, Sonogashira) cross-coupling reactions was adopted to prepare the final compounds as 7 shown in scheme 1. 2,7-Dibromo-9,9-dihexyl-9H-fluorene (1) and 2-bromo-9,9-dihexyl-9H-8 fluorene (2) were obtained by a C9 alkylation reaction of the corresponding starting reagents with 9 NatBuO, KI in THF. 9,9-Dihexyl-N2,N7,N7-tetrakis(4-methoxyphenyl)-9H-fluorene-2,7-10 diamine (I) and 4-(9,9-dihexyl-9H-fluoren-2-yl)-N,N-bis(4-methoxyphenyl)aniline (IV) were prepared from compound 1 and compound 2, respectively, which were reacted with bis(4-11 methoxyphenyl)amine, in the Buchwald-Hartwig reaction conditions, in the presence of 12 13 bis(dibenzylideneacetone)palladium (Pd(dba)₂) and tri-*tert*-butylphosphine (P(t-Bu)₃) as catalytic system, NatBuO as the base, in a microwave reactor. By the Suzuki-Miyamura cross-coupling was 14 15 syntesized 4,4'-(9,9-dihexyl-9H-fluorene-2,7-diyl)bis(N,N-bis(4-methoxyphenyl)aniline) (II), by 16 reacting 2,2'-(9,9-dihexyl-9H-fluorene-2,7-diyl)bis(1,3,2-dioxaborinane) with 4-bromo-N,N-bis(4methoxyphenyl)aniline (3), in the presence of tetrakis(triphenylphosphine)palladium(0) 17 (Pd(PPh₃)₄) as the catalyst, Na₂CO₃ 2M as the base, in a mixture of toluene:ethanol:H₂O (1:05:05, 18 19 v:v:v). The same procedure was also used to prepare 4-(9,9-dihexyl-9H-fluoren-2-yl)-N,N-bis(4methoxyphenyl)aniline (V), by reacting compound 2 with 4-methoxy-N-(4-methoxyphenyl)-N-(4-20 21 (4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)aniline (6). 4,4'-((9,9-Dihexyl-9H-fluorene-22 2,7-diyl)bis(ethyne-2,1-diyl))bis(N,N-bis(4-methoxyphenyl)aniline) (III) and 4-((9,9-dihexyl-9H-23 fluoren-2-yl)ethynyl)-N,N-bis(4-methoxyphenyl)aniline (VI) were prepared in the Sonogashira 24 reaction conditions, by reacting 1 and 2 with compound 5, respectively, using $Pd(PPh_3)_2Cl_2/Ph_3P$ and CuI as the catalytic system, in a mixture of anhydrous dimethylformamide (DMF) and 25 (5:1), 26 triethylamine (Et_3N) irradiation. 4-Bromo-N,N-bis(4under microwave

1	methoxyphenyl)aniline (3) was prepared by reacting bis(4-methoxyphenyl)amine with 4-
2	bromoiodobenzene, in presence of tris(dibenzylideneacetone)palladium chloroform
3	(Pd ₂ (dba) ₃ ·CHCl ₃) and 1,1'-bis(diphenylphosphino)ferrocene (dppf) as catalytic system, NatBuO as
4	the base, in toluene. To achieve compound 4 we reacted compound 3 with 2-methyl-3-butyn-2-ol in
5	presence of bis(triphenylphosphine)palladium(II) dichloride (Pd(PPh ₃) ₂ Cl ₂) copper iodide (CuI) and
6	triphenylphosphine (Ph ₃ P), as catalytic system, in piperidine. Afterwards, compound 4 was
7	deprotected with potassium hydroxide (KOH) in isopropanol to yield 4-ethynyl-N,N-bis(4-
8	methoxyphenyl)aniline (5). 4-Methoxy-N-(4-methoxyphenyl)-N-(4-(4,4,5,5-tetramethyl-1,3,2-
9	dioxaborolan-2-yl)phenyl)aniline (6) was synthesized from compound 3, treated with n-butyllitium
10	(n-BuLi) in anhydrous tetrahydrofurane (THF) at -78°C and following was added 2-isopropoxy-
11	4,4,5,5-tetramethyl-1,3,2-dioxaborolane. Detailed synthetic protocols and product characterization
12	data of all new compounds are reported in the experimental section and Supporting Information.
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1 2.2 Neutral state photophysical properties

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The photophysical properties of all the samples (I-VI) have been studied in solvents with different polarity (increasing dielectric constant: MCH < THF < DCM < ACN < DMSO), in order to investigate the effect of the environment on their optical properties.

Figs. 2a-3a show the absorption profiles in DCM (those obtained in other solvents are reported in the ESI section, Figs. S1-S8), while the photophysical data are reported in Table 1. They are characterized by two bands in the UV and blue range (c.a. 250-450 nm) that can be mainly assigned to $\pi - \pi^*$ and partial charge transfer (CT) transitions, respectively. [54] TD-DFT calculations confirm this assignment (see Table2) showing, in particular, that the higher level bands always corresponds to a CT excitation, while those at longer wavelength originate by both $\pi - \pi^*$ and CT excitations.

For MV compounds I-III, the increase of the absorption intensity (I < II < III, Table 1) can be
ascribed to the increasing conjugation (phenyl and phenylethynyl rings, see scheme 1). The same
trend is found for compounds IV-VI.

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Fig. 2 a) Absorption and b) Emission spectra of I, II and III in DCM, at room temperature.



4 Fig. 3 a) Absorption and b) Emission spectra of VI, V and VI in CH₂Cl₂, at room temperature.

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For the sample, the absorption spectra are not or slightly affected by the solvent polarity given the low polarization of the ground state (see Table 1).

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By contrast, the emission profiles (Figs. 2a-3b) reveal a substantial red shift (up to c.a. 130 nm for **III**) by increasing the solvent polarity (see Table 1). This indicates that a significant charge transfer contribution to the emission is present, in particular for samples with longer spacers (phenylethynyl: **III** and **VI** or phenyl: **II** and **V**) that show larger effect than **I** and **IV**. This trend is also confirmed by the Stokes-shift parameters (see Table 1), thus highlighting the ability of the spacer to act as a CT tuner.

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Sample	Solvent	λ_{abs}/nm	$\epsilon / M^{-1} cm^{-1}$	λ_{em}/nm	$\Delta\lambda/nm^{a}$	Φ_{PL}	τ/ns
	MCH	385	35.638	405	20	0.38	1.0
Ι	THF	383	34.355	411	28	0.48	1.5
	DCM	385	45.807	417	34	0.41	1.3
	ACN	370	41.410	422	52	0.53	1.7
	DMSO	378	31.148	422	44	0.70	3.3
	MCH	373	68.093	419	46	0.89	1.0
Π	THF	378	66.516	456	78	0.72	1.9
	DCM	376	64.960	464	88	0.92	2.2
	ACN	373	72.759	497	124	0.71	2.7
	DMSO	380	52.143	496	116	0.83	3.3
	MCH	390	90.525	424	34	0.90	0.9
III	THF	395	83.053	475	80	0.71	2.1
	DCM	395	86.560	491	96	0.65	2.4
	ACN	391	84.704	555	164	0.19	1.3
	DMSO	397	81.445	535	138	0.23	1.7
	MCH	344	24.431	394	50	0.16	1.0
IV	THF	345	22.916	441	96	0.39	2.2
	DCM	345	22.362	431	86	0.41	1.7
	ACN	341	22.825	441	100	0.40	3.3
	DMSO	345	22.917	441	96	0.67	4.0
	MCH	348	33.834	408	60	0.40	1.1
V	THF	352	31.944	456	104	0.81	2.8
	DCM	348	35.123	472	124	0.89	3.0
	ACN	348	35.866	501	153	0.60	3.6
	DMSO	355	34.252	496	141	0.75	4.5
	MCH	366	39.422	412	46	0.51	1.0
VI	THF	368	40.748	472	104	0.97	2.6
	DCM	368	40.406	479	111	0.65	2.8
	ACN	364	39.611	522	158	0.47	2.6
	DMSO	368	39.615	524	156	0.52	3.1

Table 1. Photophysical properties of compounds I-VI in solution at room temperature.

2 a ss = Stockes shift

4 Most of the samples shows remarkable photoluminescence efficiencies (up to > 90%) under
5 different polarity environment. The corresponding decays range from c.a. 1 to 4 nanosecond (Table

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1 1), indicating a gradual increase of the CT character by passing from MCH up to DMSO and ACN,

2 as a consequence of the larger stabilization of the charge transfer levels in polar media.

- 3
- 4 Table 2. Absorption energies, oscillator strengths (o.s), main single-particle transitions, and
 5 character

	Energy (nm)	0.S.	Character
Ι	362	0.73	СТ
	293	0.17	π-π*
	292	0.36	СТ
	291	0.10	СТ
II	383	0.85	СТ
	286	0.21	π-π *
III	421	0.94	СТ
	315	0.25	π-π *
	305	0.41	СТ
IV	334	0.66	СТ
	287	0.23	π-π *
	278	0.09	СТ
	220	0.21	СТ
V	354	0.72	СТ
	283	0.32	π-π *
VI	382	0.80	СТ
5	301	0.36	π-π *
	280	0.29	СТ

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8 2.3 Electrochemical characterization

9 Cyclic voltammograms, show reversible oxidations in the potential window between +0 and 1.2 V
10 *vs*. Ag/AgCl (Figs. 4a-c, Fig. S10 and Table 3). Specifically, two reversible one-electron oxidations
11 can be observed for compound I, while the monoamines (IV-VI) and the compounds II and III
12 show a one-reversible oxidation wave. The monoamines (IV-VI), reference compounds, show a
13 very similar behavior, characterized by redox processes occurring at 0.69 V, 0.77 V and 0.74 V for
14 IV, V and VI, respectively, indicating that the length of the π-conjugation does not significantly

influence the oxidative process. The two redox processes for compound I, ascribed to the radical 1 cation/neutral $(N^{\bullet+/0})$ and dication/radical cation $(N^{++/\bullet+})$ couples, are separated by a potential 2 splitting of 342.6 mV, suggesting a strong coupling among the amine centers (Table 4). The 3 stability of the radical cation species $(\mathbf{I}^{\bullet+})$ is clearly evidenced by the lower value of the first 4 oxidative potential when compared with the reference monoarylamine ($IV^{\bullet+}$) (0.57 V vs 0.69 V). A 5 6 very different situation is found in the CVs of compound **II** and **III**, where only one redox process 7 is detectable. In order to better resolve the two oxidation processes, a DPV analysis was performed. 8 For compound **II** the DPV clearly shows two distinctive processes separated by a potential splitting of 72 mV (Fig. S9); while, for compound III the two oxidation processes were hardly 9 distinguishable. The oxidative potential of **II** and its reference monoarylamine **V** is almost the same 10 (0.76 V vs 0.77 V), suggesting a weak electron coupling between the two redox centers. This is a 11 typical example of "potential compression". [55, 56]. The redox process of III occurs at 80 mV 12 more positive than the reference monoarylamine, VI. In this case, therefore, the oxidation process 13 can be considered as n one-step two-electron process, at least from a thermodynamic point of view. 14 15 As we will see shortly, this could be an example of the so-called "potential inversion", [55, 56] for 16 which the structural rearrangements associated with the one-electron oxidation causes a high instability of the radical cation with respect to the neutral and dicationic species. From the data 17 reported above, we note that the increase of the distance between the redox centers, within the series 18 19 **I-III**, causes a destabilization of the radical cation, resulting in a shift towards higher potentials of the first oxidation. 20



- **1** Fig. 4. Cyclic voltammetry of I (a) (50 mV/s); II (b) (50 mV/s); III (c) (50 mV/s) at $c = 10^{-3}$ M in
- $\label{eq:ch2} 2 \qquad CH_2Cl_2/TBAPF_6~(0.1~M)~\textit{vs}~AgCl/Ag.$
- **3 Table 3.** Electrochemical Properties and Corresponding Energy Levels^a

	$E_{1/2}(1)$ (mV)	$E_{1/2}(2) (mV)$	${}^{\mathrm{b}}\Delta\mathrm{E}_{1}$	^с Е _{номо}	^d E _{LUMO}	$E_{g}^{opt}(eV)$
			(mV)	(eV)	(eV)	0
Ι	-9.2	333.4	342.6	-5.08	-2.25	2.83
II	190.5	262.5	72	-5.26	-2.31	2.95
III	267.1	/	/	-5.35	-2.32	3.03
IV	189.1	/	/	-5.28	-2.08	3.20
V	132	/	/	-5.35	-2.2	3.14
VI	242.8	/	/	-5.33	-2.28	3.05

4 ${}^{a}c = 1 \times 10^{-3} \text{ mol/L in CH}_{2}Cl_{2}/TBAPF_{6} (0.1 \text{ M}) \text{ vs. Fc}^{+}/Fc \text{ at } 50 \text{ mV/s.} {}^{b}\Delta E = E_{1/2}(2) - E_{1/2}(1).$ 5 ${}^{c}E_{HOMO} = -(E_{onset(ox1)} + 5.16) \text{ (eV). } {}^{d}E_{LUMO} = E_{g}^{opt} - E_{HOMO}$

- 6 7
- 8 2.4 Vis/NIR spectra of radical cation species

9 The radical cations of compounds I-VI were generated upon oxidation in stepwise additions of antimony pentachloride (SbCl₅) (Fig. 5 and Fig. S11) and copper perchlorate (CuClO₄) (Figs. S12-10 S14) in CH₂Cl₂ and MeCN solutions, respectively, and their UV/vis/NIR changes were 11 investigated. In addition, the electrochromic and electrofluorochromic properties of compounds I-12 investigated by spectroelctrochemical experiments 13 III were also in CH₂Cl₂ and tetrabutylammonium hexafluorophosphate (TBAPF₆) as supporting electrolyte. (See Fig. S15). 14

All MV compounds show the rise of a broad absorption band in the range 4000-9000 cm⁻¹ which is associated with an optically induced hole transfer, IV-CT, from the oxidized arylamine moiety to the second neutral arylamine unit. For compound I^+ this band is rather intense and broad, well separated from the adjacent radical bands, and centered at 6590 cm⁻¹; instead, for the compounds II^+ and III^+ the IV-CT (at 7592 cm⁻¹ and 8536 cm⁻¹, respectively) displays a weaker intensity than for I^+ and an evident overlap with other radical bands, in particular for compound III^+ . An analogous behavior is nicely observed during the electrochemical oxidation of the above

compounds (Fig. S15). Actually, the spectroelectrochemical experiment combined with the CVs 1 (Fig. 4) allowed us to clearly assign the bands of the radical cation and dication species generated at 2 the working electrode from the neutral species of I and II, while, it was not possible to do the same 3 for compound **III**, because the IV-CT band of its radical cation was hardly detectable. However, as 4 previously shown this band appears of very low intensity and overlapped with the band of the 5 dication species, due to its strong shift to higher energy in the absorption spectra. The weak 6 7 intensity of the IV-CT bands of \mathbf{II}^+ and \mathbf{III}^+ , is probably due to the low oscillator strengths of the 8 associated excitations, indicating a weak electronic coupling (see Table 4).



Fig. 5 Absorption spectra of I (a) $(1.3 \times 10^{-5} \text{ M})$, II (b) $(1.7 \times 10^{-5} \text{ M})$, III (c) $(1.7 \times 10^{-5} \text{ M})$ and VI (d) $(1.8 \times 10^{-5} \text{ M})$ in CH₂Cl₂ while adding dropwise a solution of SbCl₅ in CH₂Cl₂ (1 mM).

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- 1 2
- 3
- 4

5 Table 4 Absorption energies, oscillator strengths (o.s), main single-particle transitions, and
6 character

	Energy	0.S.	Character
\mathbf{I}^+	6627	0.803	IVCT
	17825	0.11	BNCT
	23041	0.55	LRCT
\mathbf{II}^+	5627	0.10	IVCT
	11919	0.32	BNCT
	15083	0.29	π – π *
	22727	0.13	LRCT
\mathbf{III}^+	5733	0.09	IVCT
	10977	0.44	BNCT
	14881	0.29	π–π*
	20449	0.28	LRCT
	2341	0.740	LRCT
IV^+	13624	0.37	BNCT
	15480	0.26	π – π *
	24630	0.16	LRCT
\mathbf{V}^{+}	11468	0.42	BNCT
	15083	0.29	π – π *
	27027	0.23	LRCT
\mathbf{VI}^+	10616	0.55	BNCT
	14925	0.29	π – π *
	19417	0.20	LRCT
	24331	0.13	LRCT

- 8
- 9

10 The assignment of the IV-CT transition character is supported by the Vis/NIR measurements of 11 reference compounds **IV**⁺-**VI**⁺, which do not show low energy transitions at the same energy 12 frequency in oxidized forms (Fig. 6d and Fig. S11), as well as by the fact that the IV-CT band 13 disappears when the dication species are generated. A further confirmation for the nature of this

low-energy band comes from the analysis of the TD-DFT density difference plots (Fig. 6), that 1 2 shows the variation of the electron density upon excitation. For all compounds, in fact, the 3 excitation involves a charge transfer between the two redox centers. Note anyway that in going 4 from \mathbf{I}^+ to \mathbf{III}^+ , an increasing charge separation is observed upon excitation. This is quantitatively described by the ratio between ΔR ,[57] i.e. the distance of centers of the excited- and ground-state 5 6 charge densities, and ΔNN , the geometric distance between the N atoms in the redox centers; at the 7 TD-DFT level of theory the ratio is computed to be 0.11, 0.90 and 0.92 for \mathbf{I}^+ , \mathbf{II}^+ , and \mathbf{III}^+ , 8 respectively. This trend suggests that the coupling between the redox centers is diminishing in the series I^+ to III^+ . 9

10



- 11
- 12

13 Fig. 6 TD-DFT density difference plots for the lowest energy excitation of radical compounds I^+ -

14 **III**⁺. The blue regions denote an increase of electron density upon excitation; the red regions denote

15 a depletion of electron density upon excitation.

1	In addition to the IV-CT band, in all radical species a band is observable at about 20000 cm ⁻¹ , that is
2	due to long-range charge-transfer excitations (LR-CT). For all MV species an absorption band is
3	recorded between 10500 cm ⁻¹ and 13000 cm ⁻¹ and it is associated with the hole transfer from the
4	oxidized arylamine to the bridge (BN-CT), see Table 5. This transition band for radical \mathbf{I}^{+} is not
5	present, it starts to rise upon the second oxidation with the generation of the \mathbf{I}^{2+} (see isosbestic point
6	9860 cm ⁻¹). For compounds \mathbf{II}^+ and \mathbf{III}^+ the NB-CT band appears already during the first oxidation
7	process (before the addition of an equivalent of oxidant) and continues to grow during the second
8	oxidation step with the formation of \mathbf{II}^{2+} and \mathbf{III}^{2+} species, respectively. These absorption bands are
9	also present, at the same energy frequencies, into vis/NIR spectra of reference compounds V^+ - VI^+ .
10	In addition to the IV-CT and the bridge band, all MV species, as well as the monoarylamine radical
11	cations, exhibit an additional transition band attributes to π - π * transition typical of arylamine
12	radical cations which lies in the range 13000-16000 cm ⁻¹ . In order to analyze in detail the IV-CT
13	band of the various compounds and identify the class to which the MV belong, a quantitative
14	analysis of the IV-CT band was performed by adapting the experimental spectra with Gaussian
15	functions and extrapolating the main parameters that characterize it (Figs. S16-S17). All the IV-CT
16	parameters are collected in Table 5.

17	Table 5 Band shape data of the IV-CT band of \mathbf{I}^+ \mathbf{II}^+ and \mathbf{III}^+
1/	

		${}^{a}\mathrm{CH}_{2}\mathrm{Cl}_{2}$							^b MeCN
	$\tilde{v}_{max} \in [M^{-1}cm^{-1}]$ $cv_{1/2}(HTL)$ $\tilde{v}_{1/2}(high)$ $\tilde{v}_{1/2}(obs)$ $\tilde{v}_{1/2}(low)$ $\tilde{v}_{1/2}(high)/$ $\tilde{v}_{1/2}(high)/$							v_{max}	
	$[cm^{-1}]$		$[cm^{-1}]$	$[\mathrm{cm}^{-1}]^a$	$[cm^{-1}]^{b}$	$[cm^{-1}]^{c}$	$\tilde{v}_{1/2}(\text{low})$	$\tilde{v}_{1/2}(\text{HTL})$	$[cm^{-1}]$
\mathbf{I}^+	6590	42919	3902	3524	2936	2348	1.50	0.90	7336
\mathbf{II}^+	7592	10960	4188	4766 ^d	4766 ^d	4766 ^d	1.00^{d}	1.14 ^d	9099
III^+	8536	9309	4440	4673 ^d	4673 ^d	4673 ^d	1.00^{d}	1.06^{d}	10126

^a Acquired using chemical oxidation with SbCl₅. *b* Acquired using chemical oxidation with
CuClO₄. ^c Calculated according to eq 1.

20

For I⁺ only one Gaussian function was employed, while for II⁺ and III⁺, due to the overlap with the
adjacent radical band (Fig. S14), a deconvolution with three Gaussian functions was required to

obtain a satisfactory fit (Figs. S16-S17). The spectra used for the band fits were those obtained after addition of ca 0.25 equiv. of oxidizing agent, in order to minimize overlap with dication bands and avoid disproportionation of the mixed-valence state.[38, 58] Given the amount of added oxidant, the molar absorptivities were calculated considering that all of the oxidant added resulted in the formation of the monocation. The observed width of the IV-CT band ($\dot{v}_{1/2[obs]}$) was compared with that expected from Hush theory for class-II compounds, $\dot{v}_{1/2[Hush]}$ eq. 1,

7
$$\dot{v}_{1/2[Hush]} = \sqrt{2310 \times \dot{v}_{max}}$$
 (1)

8 where both the $\dot{\nu}_{1/2[Hush]}$ and $\dot{\nu}_{max}$ are given in cm⁻¹.

The asymmetry of the IV-CT band was estimated by the ratio $\dot{v}_{1/2[High]} / \dot{v}_{1/2[low]}$, where $\dot{v}_{1/2[high]}$ 9 and $\dot{v}_{1/2[low]}$ are twice the half-width on high- and low-energy side of the band, respectively. For \mathbf{I}^+ 10 $\dot{v}_{1/2[obs]}$ is narrower than $\dot{v}_{1/2[Hush]}$ and the IV-CT band shows an evident asymmetry (Fig. S16), 11 these parameters commonly belong to class III or mixed-valence compounds borderline of class 12 II/III. More specifically, for I⁺ the ratio $\dot{v}_{1/2[High]} / \dot{v}_{1/2[low]}$ value is 1.50, comparable to other values of 13 class III systems, therefore we can assign I⁺ to class III. [33] For II⁺ and III⁺ $\dot{\nu}_{1/2[obs]}$ are slightly broader 14 than the Hush limit and $\dot{v}_{1/2[high]}$ are larger $\dot{v}_{1/2[Hush]}$; thus, these IV-CT parameters support the 15 assignment of \mathbf{II}^+ and \mathbf{III}^+ to class II. [33, 38, 59] [28] As a further test to determine the class of 16 MV compounds, the solvent-dependence of the IV-CT was estimated recording the oxidation 17 experiments in two different solvents, CH_2Cl_2 and MeCN. The IV-CT of I^+ showed a modest blue 18 shift of 746 cm⁻¹, while the IV-CT of \mathbf{II}^+ and \mathbf{III}^+ exhibited a more significant hypsochromic shift 19 of ca. 1507 and 1590 cm⁻¹, respectively. This proves that, the latter systems show a more localized 20 charge with respect to \mathbf{I}^+ , and therefore the IV-CT is shifted to higher energies due to the increase of 21 the solvent reorganization energy in MeCN vs CH_2Cl_2 (Pekar factor $\gamma_{MeCN} = 0.526$ and $\gamma_{DCM} =$ 22 0.381).[60] As expected for MV systems with a larger charge delocalization, \mathbf{I}^{+} , the 23 solvatochromism is less prominent. 24

2 2.5 Electron Coupling

3 The electron coupling, *V*, between diabatic states in MV systems was estimated, according to the
4 Mulliken-Hush theory, from the equation:

5
$$V = \frac{\tilde{v}_{max}\mu_{ge}}{eR}$$
(2)

6 where μ_{ge} is the transition dipole moment (in Debye) and $\tilde{\nu}_{max}$ is the absorption maximum of the IV-7 CT, *e* is the electronic charge and *R* (in Å) is effective electron-transfer distance.

8 For class-III systems, the coupling can also be estimated directly by the formula

9
$$V = \frac{\tilde{\nu}_{max}}{2}$$
(3)

10 About the R value in equation 2, several studies report that the effective electron coupling distance 11 does not correspond to the geometrical distance between redox centers (N-N), especially in MV 12 systems where the charge is more delocalized. The R value can be estimated by either Stark 13 spectroscopy or via semiempirical calculations. In this work, we will consider for the *R* value both 14 N-N geometrical distance (R_{NN}) and R_{ab} estimated by the following equation (Ref):

15
$$R_{ab} = \sqrt{\frac{\Delta \mu_{ab}^2 + 4\mu_{ge}^2}{e}}$$
(4)

where μ_{ge} is the adiabatic transition moment (experimental or calculated) and $\Delta \mu_{ab}$ is the adiabatic 16 dipole moment difference. Since $\Delta \mu_{ab}$ is difficult to measure experimentally, we used DFT 17 computed adiabatic moment differences.[31] The estimate of the electron coupling V_{NN} and V_{ab} 18 19 (Table5) has been made by the eq 2, for the three MV systems using the N-N geometric distance (R_{NN}) and the R_{ab} values, respectively, and considering experimental value of μ_{ge} and ν_{max} from 20 Table 6. The equation 3 has been applied only for \mathbf{I}^+ compound, because it is the only one that 21 belongs to class III. As expected from previous discussion we find that the electron coupling 22 increases in the series $III^+ < II^+ < I^+$. 23

Table 6 Transition dipole moment ($\mu_{ge}(D)$, Diabatic electron transfer, Nitrogen-Nitrogen, distance (R_{NN}), Estimated adiabatic electron-transfer distance (R_{ab}), Electron coupling, V, calculated according to equation 2 and according the equation 3 (for class-III species).

Compounds	$\mu_{ge}(D)$	$\boldsymbol{R}_{NN}\left(\mathrm{\AA} ight)$	R_{ab} (Å)	$V_{NN}(cm^{-1})$	$V_{ab}(cm^{-1})$	V eq 3
						(cm ⁻¹)
\mathbf{I}^{+}	15.75	9.60	6.67	2252	3228	3295
\mathbf{II}^+	8.15	18.13	10.21	764	1257	-
III ⁺	6.81	23.14	10.64	523	1134	-

6

7 2.6 Chemical fluorescence switching and electrofluorochromism

All compounds are good emissive materials with high quantum yield. They show fluorescence in 8 9 the blue and green range, due to the molecular extended π -conjugation and to intramolecular charge-transfer processes. The fluorescence quenching experiments by chemical oxidation were 10 11 carried out in order to investigate the contribution of the electron-coupling between the redox centers to the fluorescence quenching (Fig. 7 and Figs. S18-S21). As known, the light emission of 12 13 arylamine derivatives is quenched by generation of their radical species.[13, 61-63] Through 14 chemical oxidation with SbCl₅ in CH₂Cl₂, and analyzing the decrease of fluorescence intensity by linear fitting as a function of the amount of oxidant added, we observed that the presence of two 15 16 interacting redox centers further affects the fluorescence quenching. This effect is particularly evident for compound I, in which a stronger interaction between the redox centers is present. 17 Comparing the fluorescence quenching trend of I and IV (Figs. 7a-b), we observe that I shows a 18 larger linear-slope grade than IV (Fig. 7c). 19



Fig. 7 Fluorescence emission spectra (a) of I (ca 2×10^{-5} M in CH₂Cl₂) and (b) of IV (ca 2×10^{-5} M) 3 4 upon SbCl₅ titration. (c) Correlation of fluorescent quenching trend of **I** (red line) and **IV** (blue line) vs. equivalent SbCl₅ added. 5

7 The above-mentioned studies have been carried out by exciting I and IV at 345 and 342 nm (isosbestic point), respectively. Compounds II, III, V and VI also show a fluorescence quenching 8 9 upon oxidation process although, the fluorescent variation trend for II and III is comparable with V 10 and VI compounds, probably due to the relatively weak electron coupling between the redox 11 centers in these compounds. We have also monitored the fluorescence variation of the 12 bisdiarylamine and monodiarylamine systems in CH₂Cl₂ solutions as a function of the voltages (vs AgCl/Ag). In the system I the fluorescence is almost constant up to about 0.6 V but, above this 13 14 value, a stepwise increase of the contrast ratio occurs (Fig. 8a) which increases with the voltage, as already observed in the similar compound 9,9-bis(2-(2-methoxyethoxy)ethyl)- N^2 , N^7 , N^7 -15

tetrakis(4-methoxyphenyl)-9H-fluorene-2,7-diamine.[13]. In the homologous monoamine system 1 2 (IV), a significant fluorescence quenching (high contrast ratio) is observed only at voltages close to 3 the fluorene oxidation, that is, for potential values larger than that leading to the radical cation. The last observation is also shared by the other two monoamine systems (Figs. 8b-c). In II and III, 4 5 where there is not a clear potential splitting, fluorescence quenching occurs in correspondence to 6 potential values at which both mono and dication species are quite simultaneously generated (Figs. 7 4b-c). It is therefore clear that, for practical applications in electrofluorochromism, it is convenient 8 to use a coupled system like I because a) a significant contrast ratio is achieved at low voltages and 9 b) the quenching process is fully reversible.



10

11

12 **Fig.8** Fluorescence contrast ratio as a function of the applied voltage.

- 14
- 15

1 3. CONCLUSIONS

2 We have synthesized six diarylaminofluorene–based compunds, three with D- π -D (I-III) structure 3 and three with D- π (IV-VI) structure. The D- π systems have been used as model compounds for their symmetric diarylamine homologous, in order to better characterize the electronic transitions in 4 5 the D- π -D systems. The correlation between electronic properties, i.e. the electronic coupling between the redox centers, and the molecular structure has been investigated, focusing the study on 6 7 the mixed-valence (MV) response of the three diarylaminofluorene D- π -D radical cation derivatives 8 (I-III) with respect to the π -conjugated bridge and its length. The three MVs compounds I-III show 9 intense intervalence charge transfer (IV-CT) in the NIR region, which has been exploited to 10 quantify the electron coupling, V. All compounds showed excellent photophysical properties, such 11 as high quantum yield (up to > 90%) and high molar absorptivity of the IV-CT (up to > 40000), with the length of the π -conjugated bridge exploitable as a tool to tune their optoelectronic 12 13 properties.

All compounds exhibited chromatic switching up to NIR by varying their oxidized states. The spectroelectrochemical measurements revealed also the ability of these compounds to work as anodic components for electrochromic applications and as promising materials for energy saving. The fluorescence switching experiments by applied potential highlighted that these class of materials can modulate the light emission intensity by changing their oxidized states.

19 The above results show that these compounds are of potential use in a wide range of applications20 such as in displays, molecular logic gates, sensors and memory devices.

21

22 4. EXPERIMENTAL SECTION

23 *4.1 General Methods*

1-Bromohexane, 2-bromo-9*H*-fluorene, bis(4-methoxyphenyl)amine, 2,7-dibromo-9*H*-fluorene and
9,9-dihexylfluorene-2,7-bis(trimethyleneborate) were purchased from commercial sources (Sigma

Aldrich) and used without further purification. All solvents and reagents were used as received, 1 unless otherwise claimed. The syntheses microwave-assisted were performed with CEM Discover 2 3 Labmate reactor. The reactions were monitored by TLC using 0.25 mm silica gel plates with UV indicator (60F-254). The ¹H and ¹³C NMR spectra were recorded on a Bruker AVANCE III 400 4 MHz instrument using chloroform-d (CDCl₃) and acetone-d6 as solvents, and splitting patterns 5 6 were described as singlet (s), doublet (d), triplet (t), quartet (q) or multiplet (m). Elemental analyses 7 were done by Carlo Erba CHNS-O EA1108-Elemental Analyzer. LC-MS spectra were acquired 8 with an Agilent 6300 Series Ion Trap source (APCI).

9

4.2 UV-Vis-NIR absorption and fluorescence spectroscopy 10

UV-Vis absorption spectra were recorded on Varian-Cary 3000 spectrophotometer. For 11 luminescence experiments, the samples were placed in fluorimetric 1-cm path cuvettes. Uncorrected 12 13 emission spectra were obtained with an Edinburgh FLS980 spectrometer equipped with a peltiercooled Hamamatsu R928 photomultiplier tube (185-850 nm). An Edinburgh Xe900 450 W Xenon 14 15 arc lamp was used as exciting light source. Corrected spectra were obtained via a calibration curve 16 supplied with the instrument. Luminescence quantum yields (Φ em) in solution obtained from spectra on a wavelength scale (nm) were measured according to the approach described by Demas 17 and Crosbya using air-equilibrated [Ru(bpy)₃Cl₂ in water solution Φ em = 0.028, or quinine sulphate 18 19 Φ em = 0.546][64] as standard. Emission lifetimes in the ps-us range were determined with the 20 single photon counting technique by means of the same Edinburgh FLS980 spectrometer using a laser diode as excitation source (1 MHz, $\lambda_{exc} = 407$ nm) and a Hamamatsu MCP R3809U-50 (time 21 22 resolution 20 ps) as detector. Experimental uncertainties are estimated to be \pm 8% for lifetime determinations, \pm 20% for emission quantum yields, \pm 2 nm and \pm 5 nm for absorption and 23 24 emission peaks, respectively.

25 Redox titrations monitored by UV/Vis/NIR spectroscopy were performed in CH₂Cl₂ and ACN solvents using a Varian-Cary 5000 UV-Vis-NIR absorption spectrometer and 10×10 mm quartz-26

cuvettes with Teflon stopper (Hellma). SbCl₅ (Sigma Aldrich) and CuSO₄ (Sigma Aldrich) were

used as oxidant in CH_2Cl_2 and CAN, respectively. The bistriarylamine solution were titrated with a

3	solution of oxidant in the respective solvent (ca. 1 mM) using a microliter syringe (Hamilton).
4	
5	4.3 Computational details
6	All calculations have been performed using the TURBOMOLE program [65] [66] using the PBE0-
7	1/3 functional[67] and a def2-TZVP[68] basis set
8	
9	4.4 Electrochemistry and spectroelectrochemistry
10	Electrochemical characterization of compounds was carried out by cyclic voltammetry (CV) using a
11	AMEL s.r.l. (Mod. 7050) potentiostat. A typical three-electrode cell was assembled with a glassy
12	carbon disk-working electrode, a Pt-wire auxiliary electrode, and an Ag/AgCl non-aqueous
13	reference electrode. Cyclic voltammograms were acquired at different scan rate, from 50 to 100 mV
14	s ⁻¹ , on 1 mM compound solutions prepared in the electrolyte solution, which consisted of 0.1 M
15	tetrabutylammonium hexafluorophosphate (TBAPF ₆) in dichloromethane (CH_2Cl_2). All the
16	solutions were previously degassed with N_2 . The CV of the Ferrocenium/Ferrocene (Fc ⁺ /Fc) couple
17	(0.1 mM) was also recorded in the same condition used for the MV compounds solutions and used
18	as external reference for potential calibration. Spectroelectrochemical experiments were performed
19	performed as described elsewhere [69, 70] with an electrolytic cell (BAS Inc.) composed of a 1 mm
20	path length cuvette, where a platinum gauze thin layer and a platinum wire were used as the
21	working electrode and the auxiliary electrode, respectively. A pseudo-reference electrode consisting
22	of an Ag wire was calibrated against the Fc ⁺ /Fc redox couple. The spectroelectrochemical cell was
23	filled with dichloromethane solutions of each compound (0.5 mM) and TBAPF_6 (0.1 M). UV-vis-
24	NIR spectra were recorded using a Vertex 80 (Bruker) spectrophotometer. The potential was
25	supplied by means of an Amel 2049 model potentiostat. Measurements were performed at 25 $^{\circ}$ C.
20	

- 1 4.5 Synthetic procedures and product characterization
- 2 4.5.1 Sinthesis of 2,7-dibromo-9,9-dihexyl-9H-fluorene (1)

In a three-neck round bottom flask 2,7-dibromofluorene (1 g, 3.11 mmol), tert-BuONa (1.194 g, 3 4 12.44 mmol), KI (0.051 g, 0.311 mmol) and anhydrous THF (8 mL) were stirred for 1h under a nitrogen atmosphere. Then, bromohexane (1.30 g, 7.9 mmol) was added dropwise and the reaction 5 6 mixture was stirred overnight at reflux. The reaction mixture was cooled to rt, poured in water and 7 extracted with diethyl ether. The organic layer was washed with water and dried over anhydrous Na₂SO₄ and the solvent was evaporated under a reduced pressure. The crude residue was purified 8 by column chromatography on silica gel (eluent petroleum ether), to yield the pure product 1 as a 9 white powder (96% yield). ¹H NMR (400 MHz, CDCl₃): δ 7.52 (d, J = 7.7 Hz, 2 H), 7.47-7.44 (m, 10 4H), 1.94-1.89 (m, 4H), 1.17-1.01 (m, 12H), 0.78 (t, 6H), 0.63-0.55 (m, 4H). ¹³C NMR (100 MHz, 11 CDCl₃): δ 152.38, 138.86, 129.94, 125.97, 121.25, 120.92, 55.49, 39.99, 31.26, 29.37, 23.44, 22.37, 12 13.79. GC-MS m/z 492.2 CG/MS (EI) calcd for C₂₅H₃₂Br₂ m/z 492,09, found 492,10. Elemental 13 analysis calcd for C₂₅H₃₂Br₂: C, 60.99; H, 6.55; Br, 32.46. Found C, 60.85; H, 6.69. 14

15

16 4.5.2 Sinthesis of 2-bromo-9,9-dihexyl-9H-fluorene (2)

17 Following the same procedure of compound 1, 2-bromo-9H-fluorene (1 g, 4.1 mmol), tert-BuONa (1.57 g, 16.4 mmol) and KI (0.067 g, 0.41 mmol) were mixed in anhydrous THF (9 mL) and stirred 18 19 under a nitrogen atmosphere for 1h. Bromohexane (2.52 g, 15.3 mmol) was added dropwise and the 20 reaction mixture was stirred overnight at reflux. The reaction mixture was cooled to rt, poured in water and extracted with diethyl ether. The organic layer was washed with water and dried over 21 anhydrous Na₂SO₄ and the solvent was evaporated under a reduced pressure. The crude residue was 22 purified by column chromatography on silica gel (eluent petroleum ether), to yield the pure product 23 2 as a yellow-orange oil (96% yield). ¹H NMR (400 MHz, CDCl₃): δ 7.68-7.65 (m, 1H), 7.56 (d, J 24

= 8.67 Hz, 1H), 7.46-7.44 (m, 2H), 7.34-7.32 (m, 3H), 1.98-1.92 (m, 4H), 1.14-1.03 (m, 12H), 0.77
(t, 6H), 0.63-0.56 (m, 4H). ¹³C NMR (100 MHz, CDCl₃): δ 152.77, 150.11, 139.93, 139.82, 129.66,
127.25, 126.71, 125.92, 122.67, 120.81, 120.74, 119.53, 55.17, 40.10, 31.28, 29.45, 23.47, 22.38,
13.80. GC-MS calcd for C₂₅H₃₃Br m/z 412.18, found 412,20. Elemental analysis calcd for C₂₅H₃₃Br: C, 72.63; H, 8.05; Br, 19.33. Found C, 72.75; H, 8.19.

6

7 4.5.3 Sinthesis of 4-bromo-N,N-bis(4-methoxyphenyl)aniline (3)

A mixture of bis(4-methoxyphenyl)amine (3.00 g, 13.1 mmol), 4- bromoiodobenzene (4.64 g, 16.4 8 mmol), tert-BuONa (1,89 g, 19.7 mmol), Pd₂(dba)₃·CHCl₃ (0.068 g, 0.066 mmol) and dppf (1, 1'-9 bis(diphenylphosphino)ferrocene) (56 mg, 0.10 mmol) was heated in dry toluene (20 mL), under a 10 nitrogen atmosphere, at 90 °C for 24 hours. The solvent was removed under vacuum and the residue 11 12 was dissolved in dichloromethane and washed with water. The organic layer was dried over anhydrous Na₂SO₄ and the solvent removed at a reduced pressure. The crude product was purified 13 by flash chromatography on silica gel (eluent CH_2Cl_2 /petroleum ether 3/7), to yield the pure product 14 **3** as a grey solid (80% yield). Mp 96 - 98 °C. ¹H NMR (400 MHz, acetone- d_6): δ 7.29 (d, J = 8.915 Hz, 2H), 7.06 (d, J = 8.9 Hz, 4H), 6.91 (d, J = 8.9 Hz, 4H), 6.74 (d, J = 8.9 Hz, 2H), 3.79 (s, 6H). 16 ¹³C NMR (100 MHz, acetone-*d*₆): δ 156.40, 148.20, 140.00, 131.45, 126.79, 120.87, 114,65, 17 111,04, 54.64. LCMS (APCI) calcd for C₂₀H₁₈BrNO₂ [M+H⁺] 384.1, found 384.4 Elemental 18 analysis calcd for C₂₀H₁₈BrNO₂: C, 62.51; H, 4.72; Br, 20.79; N, 3.65. Found C, 62.56; H, 4.81; N, 19 20 3.58.

21

22 4.5.4 Sinthesis of 4-(4-(bis(4-methoxyphenyl)amino)phenyl)-2-methylbut-3-yn-2-ol (4)

To a solution of compound **3** (2.0 g, 5.22 mmol) in dry piperidine (16 mL) was added 2-methyl-3-

butyn-2-ol (0.658 g, 7.83 mmol). After the solution was degassed with a nitrogen flow for 30 min,

Pd(PPh₃)₂Cl₂ (37 mg, 0.052 mmol), CuI (25 mg, 0.13 mmol) and PPh₃ (272.78 mg, 1.04 mmol) 1 were added. The reaction mixture was refluxed under a nitrogen atmosphere for 10 h. The reaction 2 mixture was cooled to rt, filtered, and the precipitate was rinsed with diethyl ether, and the 3 combined filtrates were dried over anhydrous Na_2SO_4 and evaporated to dryness. The residue was 4 purified by column chromatography on silica gel (eluent ethyl acetate/petroleum ether 2/8), to yield 5 the pure product **4** as a dark syrup, (97% yield). ¹H NMR (400 MHz, Acetone- d_6): δ 7.17 (d, J = 8.96 7 Hz, 2H), 7.07 (d, J = 9.0 Hz, 4H), 6.92 (d, J = 9.0 Hz, 4H), 6.73 (d, J = 8.9 Hz, 2H), 4.36 (s, 1H), 3.79 (s, 6H), 1.50 (s, 6H). ¹³C NMR (100 MHz, Acetone- d_6): 156.52, 148.59, 139.81, 131.92, 8 127.08, 118.24, 114.64, 113.67, 93.37, 80.85, 64.00, 54.64, 31.11. LCMS (APCI) calcd for 9 C₂₅H₂₅NO₃ [M+H⁺] 388.2, found 388.4. Elemental analysis calcd for C₂₅H₂₅NO₃: C, 77.49; H, 6.50; 10 N, 3.61; O, 12.39. Found C, 77.41; H, 6.63; N, 3.51. 11

12

13 *4.5.5 Sinthesis of 4-ethynyl-N,N-bis(4-methoxyphenyl)aniline (5)*

Compound 4 (2.00 g, 5.16 mmol) and KOH powder (852 mg, 15.17 mmol) were dissolved in 2-14 15 propanol (30 mL). The reaction mixture was stirred at reflux under a nitrogen atmosphere for 2 h, then quenched in ice/water and extracted with diethyl ether. The organic layer was dried over 16 anhydrous Na₂SO₄, and the solvent removed under vacuum. The residue was purified by column 17 chromatography on silica gel (eluent ethyl acetate/petroleum ether 25/75), to yield the pure product 18 **5** as a golden vellow solid, (85% vield). ¹H NMR (400 MHz, Acetone- d_6): δ 7.26 (d, J = 8.9 Hz, 19 2H), 7.09 (d, J = 9.0 Hz, 4H), 6.93 (d, J = 9.0 Hz, 4H), 6.73 (d, J = 8.9 Hz, 2H), 3.80 (s, 6H), 3.48 20 (s, 6H). ¹³C NMR (100 MHz, Acetone- d_6): δ 159.69, 149.22,139.59, 132.49, 127.30, 117.83, 21 114.68, 112.28, 83.70, 76.26, 54.65. LCMS (APCI) calcd for C₂₂H₁₉NO₂ [M+H⁺] 330.2, found 22 23 330,6 Elemental analysis calcd for C₂₂H₁₉NO₂: C, 80.22; H, 5.81; N, 4.25; O, 9.1. Found C, 80.43; H, 6.01; N, 4.27. 24

1 4.5.6 Sinthesis of 4-methoxy-N-(4-methoxyphenyl)-N-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-

2 yl)phenyl)aniline (6)

In an oven-dried 25 mL three-neck round bottom flask, a solution of 4-bromo-N,N-bis(4-3 methoxyphenyl)aniline 3 (0,7 g, 1.82 mmol) in anhydrous THF (8 mL) was prepared under a 4 5 nitrogen atmosphere. The reaction mixture was cooled to -78°C and nBuLi (2.5 M in hexane, 2 6 mmol) was added dwopwise. The reaction mixture was kept at -78°C for 1h, then 2-isopropoxy-7 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.443 g, 2.4 mmol) was added dropwise. The reaction 8 mixture was allowed to warm to rt and stirred overnight. The mixture was poured into the water and 9 extracted with diethyl ether. The organic layer was dried over anhydrous Na₂SO₄ and the solvent evaporated under a reduced pressure, to afford a brownish oil that was purified by column 10 chromatography on silica gel (eluent hexane/ CH_2Cl_2 7/3), to yield the desired product 6 as a purple-11 brown oil (40% yield). ¹H NMR (400 MHz, Acetone- d_6) δ 7.53 (d, J = 8.7 Hz, 2H), 7.08 (d, J = 9.112 Hz, 4H) 6.93 (d, J = 9.1 Hz, 4H), 6.77 (d, J = 8.7 Hz, 2H), 3.80 (s, 6H), 1.30 (s, 12H). ¹³C NMR 13 (100 MHz, Acetone- d_6) δ 156.55, 151.41, 139.92, 135.44, 127.22, 117.44, 114.61, 82.93, 54.66, 14 24.09. LCMS (APCI) calcd for C₂₆H₃₀BNO₄ [M+H⁺] 432.2, found 432.3. Elemental analysis calcd 15 for C₂₆H₃₀BNO₄: C, 72.40; H, 7.01; B, 2.51; N, 3.25; O, 14.84. Found C, 72.62; H, 7.00; N, 3.21. 16

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19 4.5.7 Sinthesis of 9,9-dihexyl-N2,N2,N7,N7-tetrakis(4-methoxyphenyl)-9H-fluorene-2,7-diamine (I)

A microwave reactor vessel was charged with compound **1** (0.200 g, 0.406mmol), bis(4methoxyphenyl)amine (0.204 g, 0.90 mmol), *tert*-BuONa (0.128 g, 1.33 mmol) and anhydrous toluene (4 mL). The reaction mixture was degassed with argon at room temperature for 15 minutes, then Pd(dba)₂ (5 mol %, 0.012g, 0.02 mmol) and P(t-Bu)₃ (1M in toluene, 0.040 mmol) were added and the reaction mixture reacted at 110°C in a microwave reactor for 50 minutes. Upon cooling, the

1	solvent was removed under a reduced pressure and the crude product was dissolved in CH ₂ Cl ₂ and
2	washed with water. The organic layer was dried over anhydrous Na ₂ SO ₄ and the solvent evaporated
3	under a reduced pressure. The crude product was purified by column chromatography on silica gel
4	(petroleum ether/CH ₂ Cl ₂ 7/3), to yield the desired compound I as a grey solid (90% yield). ¹ H NMR
5	(400 MHz, Acetone- d_6) δ 7.50 (d, $J = 8.2$ Hz, 2H), 7.02 (d, $J = 9.0$ Hz, 8H), 7.00 (d, $J = 2.0$ Hz,
6	2H), 6.87 (d, J = 9.0 Hz, 8H), 6.83 (dd, J ₁ = 8.2, J ₂ = 2.0 Hz, 2H), 3.78 (s, 12H), 1.79-1.75 (m, 4H),
7	1.20-1.07 (m, 12H), 0.83 (t, $J = 7.1$ Hz, 6H), 0.75-0.66 (m, 4H). ¹³ C NMR (100 MHz, Acetone- d_6) δ
8	155.50, 151.28, 147.26, 141.30, 134.65, 125.44, 120.59, 119.18, 116.37, 114.37, 54.61, 54.44,
9	39.77, 31.19, 23.50, 22.11, 13.26. LCMS (APCI) calcd for $C_{53}H_{60}N_2O_4$ [M+H ⁺] 789.4, found 789.8.
10	Elemental analysis calcd for C ₅₃ H ₆₀ N ₂ O ₄ : C, 80.67; H, 7.66; N, 3.55; O, 8.11. Found C, 80.88; H,
11	7.59; N, 3.47.

12

13 4.5.8 Sinthesis of 4,4'-(9,9-dihexyl-9H-fluorene-2,7-diyl)bis(N,N-bis(4-methoxyphenyl)aniline) (II)

14 2,2'-(9,9-Dihexyl-9H-fluorene-2,7-diyl)bis(1,3,2-dioxaborinane) (400 mg, 0,786 mmol), compound 15 3 (732 mg, 1.91 mmol) and Na₂CO₃ (1.70 g, 16 mmol) were added to a mixture of toluene (8 mL), water (4 mL) and ethanol (4 mL). The mixture was degassed at room temperature under a nitrogen 16 17 flow for 2 hours, before adding Pd(PPh₃)₄ (36 mg, 0.031 mmol), then stirred at 80°C for 18 hours. The reaction mixture was concentrated under vacuum, rinsed with water and the product extracted 18 19 with dichloromethane. The organic layer was dried over anhydrous Na₂SO₄ and the solvent was 20 evaporated under a reduced pressure. The crude residue was purified by column chromatography on silica gel (hexane/CH₂Cl₂ 6/4), to yield the pure product **II** as a yellow-green solid (80% yield). ¹H 21 NMR (400 MHz, Acetone- d_6) δ 7.83 (d, J = 7.9 Hz, 2H), 7.72 (d, J = 1.2 Hz, 2H), 7.63-7.59 (m, 22 6H), 7.10 (d, J = 9.10 Hz, 8H), 6.97-6.92 (m, 12H), 3.81 (s, 12H). ¹³C NMR (100 MHz, Acetone-23 d₆) δ 156.09, 151.33, 148.07, 140.56, 139.42, 139.28, 132.94, 127.15, 126.44, 124.90, 120.30, 24 120.24, 119.70, 114.55, 54.98, 54.65, 39.95, 31.15, 23.56, 22.08, 13.12. LCMS (APCI) calcd for 25

C₆₅H₆₈N₂O₄ [M+H⁺] 941.5, found 941,8. Elemental analysis calcd for C₆₅H₆₈N₂O₄: C, 82.94; H,
 7.28; N, 2.98; O, 6.80. Found C, 83.18; H, 7.39; N, 2.79.

3

4 4.5.9 Sinthesis of 4,4'-((9,9-dihexyl-9H-fluorene-2,7-diyl)bis(ethyne-2,1-diyl))bis(N,N-bis(45 methoxyphenyl)aniline) (III)

6 A microwave vessel was charged with compound 1 (200 mg, 0.205 mmol), CuI (1.54 mg, 0.008 mmol), compound 5 (162 mg, 0.492 mmol) and a mixture 1:5 of TEA/DMF (8 mL). The mixture 7 was degassed under argon at room temperature for 10 minutes, then Pd(PPh₃)₂Cl₂ (6 mg, 0.008 8 mmol) and PPh₃ (42 mg, 0.16 mmol) were added. The reaction mixture was heated in the 9 microwave reactor at 100 °C for 50 minutes, then cooled to rt, diluted with diethyl ether and washed 10 with water. The organic layer was collected and dried over anhydrous Na₂SO₄. Removal of the 11 12 solvent under a reduced pressure resulted in a crude residue, which was purified by column chromatography on silica gel (petroleum ether/CH₂Cl₂ 6/4), to yield the desired compound III as a 13 yellow solid (75% yield). ¹H NMR (400 MHz, Acetone- d_6) δ 7.82 (d, J = 7.9 Hz, 2H), 7.58 (s, 2H), 14 15 7.50 (dd, J = 7.9, J = 1.4 Hz, 2H), 7.36 (d, J = 8.9 Hz, 4H), 7.13 (d, J = 9.0 Hz, 8H), 6.95 (d, J = 9.0Hz, 8H), 6.89 (d, J = 8.9 Hz, 4H), 3.81 (s, 12H), 2.14-2.10 (m, 4H), 1.14-1.02 (m, 4H), 0.75 (t, J =16 6.8 Hz, 6H), 0.64-0.56 (m, 4H). ¹³C NMR (100 MHz, Acetone- d_6) δ 156.75, 150.88, 149.03, 14.20, 17 139.63, 132.08, 130.22, 127.32, 125.29, 122.49, 119.90, 117.97, 114.89, 113.21, 90.23, 88.55, 18 54.99, 54.67, 39.75, 31.20, 29.20, 23.51, 22.12, 13.12. LCMS (APCI) calcd for C₆₉H₆₈N₂O₄ 19 [M+2H⁺] 990.5, found 990.1. Elemental analysis calcd for C₆₉H₆₈N₂O₄: C, 83.77; H, 6.93; N, 2.83; 20 O, 6.47. Found C, 83.89; H, 7.11; N, 2.98. 21

22 4.5.10 Sinthesis of 9,9-dihexyl-N,N-bis(4-methoxyphenyl)-9H-fluoren-2-amine (IV)

In an oven dried 25 mL three-neck round bottom flask, Pd(dba)₂ (2 mol%, 0.014 g, 0.0214 mmol)
and P(*t*Bu)₃ (1 M in hexane, 0.0484 mmol) and anhydrous toluene (7 mL) were stirred at rt under a

atmosfere for Then, compound 2 (0.500)1.21 1 nitrogen 15 min. g, mmol), bis(4methoxyphenyl)amine (0.305 g, 1.33 mmol) and tert-BuONa (0.290 g, 3.03 mmol) were added and 2 the resulting mixture was stirred at reflux for 18 hours. The solvent was removed and the crude 3 4 product was dissolved in dichloromethane and washed with water. The organic layer was dried over anhydrous Na₂SO₄ and the solvent evaporated under vacuum. The crude product was purified by 5 6 column chromatography on silica gel (eluent hexane/ CH_2Cl_2 8/2), to yield the pure product IV as a 7 yellow viscous-liquid (91% yield). ¹H NMR (400 MHz, Acetone- d_6) δ 765 (d, J = 6.9 Hz, 1H), 7.60 8 (d, J = 8.2 Hz, 1H), 7.36 (d, J = 6.8 Hz, 1H), 7.28 (dt, $J_1 = 7.4$ Hz, $J_2 = 1.3$ Hz, 1H), 7.22 (dt, $J_1 = 7.4$ Hz, $J_2 = 1.3$ Hz, 1H), 7.22 (dt, $J_1 = 7.4$ Hz, $J_2 = 1.3$ Hz, 1H), 7.22 (dt, $J_1 = 7.4$ Hz, $J_2 = 1.3$ Hz, 1H), 7.22 (dt, $J_1 = 7.4$ Hz, $J_2 = 1.3$ Hz, 1H), 7.22 (dt, $J_1 = 7.4$ Hz, $J_2 = 1.3$ Hz, 1H), 7.22 (dt, $J_1 = 7.4$ Hz, $J_2 = 1.3$ Hz, 1H), 7.22 (dt, $J_1 = 7.4$ Hz, $J_2 = 1.3$ Hz, 1H), 7.22 (dt, $J_1 = 7.4$ Hz, $J_2 = 1.3$ Hz, 1H), 7.22 (dt, $J_1 = 7.4$ Hz, $J_2 = 1.3$ Hz, 1H), 7.22 (dt, $J_1 = 7.4$ Hz, $J_2 = 1.3$ Hz, 1H), 7.22 (dt, $J_1 = 7.4$ Hz, $J_2 = 1.3$ Hz, 1H), 7.22 (dt, $J_1 = 7.4$ Hz, $J_2 = 1.3$ Hz, 1H), 7.22 (dt, $J_1 = 7.4$ Hz, $J_2 = 1.3$ Hz, 1H), 7.22 (dt, J_1 = 7.4 Hz, $J_2 = 1.3$ Hz, 1H), 7.22 (dt, J_1 = 7.4 Hz, $J_2 = 1.3$ Hz, 1H), 7.22 (dt, J_1 = 7.4 Hz, $J_2 = 1.3$ Hz, 1H), 7.22 (dt, J_1 = 7.4 Hz, $J_2 = 1.3$ Hz, 1H), 7.22 (dt, J_1 = 7.4 Hz, $J_2 = 1.3$ Hz, 1H), 7.22 (dt, J_1 = 7.4 Hz, $J_2 = 1.3$ Hz, 1H), 7.22 (dt, J_1 = 7.4 Hz, $J_2 = 1.3$ Hz, 1H), 7.22 (dt, J_1 = 7.4 Hz, $J_2 = 1.3$ Hz, 1H), 7.22 (dt, J_1 = 7.4 Hz, $J_2 = 1.3$ Hz, 1H), 7.22 (dt, J_1 = 7.4 Hz, $J_2 = 1.3$ Hz, 1H), 7.22 (dt, J_1 = 7.4 Hz, $J_2 = 1.3$ Hz, 1H), 7.22 (dt, J_1 = 7.4 Hz, $J_2 = 1.3$ Hz, 1H), 7.22 (dt, J_1 = 7.4 Hz, $J_2 = 1.3$ Hz, $J_2 = 1.3$ Hz, 1H), 7.22 (dt, J_1 = 7.4 Hz, $J_2 = 1.3$ Hz, $J_2 = 1.$ 9 7.4 Hz, $J_2 = 1.3$ Hz, 1H), 7.05-7.03 (m, 5H), 6.89 (d, J = 9.1 Hz, 4H), 6.86 (dd, $J_1 = 8.2$ Hz, $J_2 = 1.3$ Hz, 1H), 7.05-7.03 (m, 5H), 6.89 (d, J = 9.1 Hz, 4H), 6.86 (dd, $J_1 = 8.2$ Hz, $J_2 = 1.3$ Hz, 1H), 7.05-7.03 (m, 5H), 6.89 (d, J = 9.1 Hz, 4H), 6.86 (dd, $J_1 = 8.2$ Hz, $J_2 = 1.3$ Hz, 1H), 7.05-7.03 (m, 5H), 6.89 (d, J = 9.1 Hz, 4H), 6.86 (dd, $J_1 = 8.2$ Hz, $J_2 = 1.3$ Hz, 1H), 7.05-7.03 (m, 5H), 6.89 (d, J = 9.1 Hz, 4H), 6.86 (dd, $J_1 = 8.2$ Hz, $J_2 = 1.3$ Hz, 2.1 Hz, 1H), 3.79 (s, 6H), 1.98-1.82 (m, 4H), 1.18-1.03 (m, 12H), 0.79 (t, 6H), 0.72-0.57 (m, 4H). 10 ¹³C NMR (100 MHz, Acetone- d_6) δ 155.66, 151.50, 150.01, 148.24, 141.18, 141.03, 134.38, 11 126.57, 125.73, 125.67, 122.39, 120.24, 119.97, 118.56, 116.06, 114.42, 54.62, 54.55, 39.83, 31.18, 12 13 29.20, 23.46, 22.09, 22.08, 13.18. LCMS (APCI) calcd for C₃₉H₄₇NO₂ [M+H⁺] 562.4, found 562.6. Elemental analysis calcd for C₃₉H₄₇NO₂: C, 83.38; H, 8.43; N, 2.49; O, 5.70. Found C, 83.52; H, 14 15 8.49; N, 2.44.

16

17 *4.5.11 Sinthesis of 4-(9,9-dihexyl-9H-fluoren-2-yl)-N,N-bis(4-methoxyphenyl)aniline (V)*

A 50 mL three-neck round bottom flask was charged with Na₂CO₃ (1.44 g, 13.6 mmol), H₂O (3.5 18 19 mL) and ethanol (3.5 mL), compound **2** (0.280 g, 0.677 mmol), compound **6** (0.320 g, 0.742 mmol) 20 and toluene (7 mL). The mixture was degassed at room temperature under a nitrogen flow for 2 hours, before adding Pd(PPh₃)₄ (0.008 g, 0.009 mmol) and then stirred at 80°C for 36 hours. 21 Toluene was evaporated and the crude product was rinsed with CH₂Cl₂ and washed with water. The 22 23 organic layer was dried over anhydrous Na₂SO₄ and the solvent evaporated under a reduced pressure. Purification by column chromatography (hexane/CH₂Cl₂ 8/2) afforded the pure product V 24 as a light yellow solid (56% yield). Mp: 109-111°C ¹H NMR (400 MHz, Acetone- d_6) δ 7.81 (d, J = 25

7.9 Hz, 1H), 7.80-7.78 (m, 1H), 7.70 (d, J = 1.5 Hz, 1H), 7.61-7.56 (m, 3H), 7.46-7.44 (m, 1H), 1 7.36-7.29 (m, 2H), 7.08 (d, J = 8.9 Hz, 4H), 6.95 (d, J = 8.7 Hz, 2H), 6.93 (d, J = 8.9 Hz, 4H), 3.80 2 (s, 6H), 2.17-2.07 (m, 4H), 1.14-0.97 (m, 12H), 0.73 (t, 6H), 0.68-0.59 (m, 4H). ¹³C NMR (100 3 MHz, Acetone-*d*₆) δ 156.09, 151.05, 150.50, 148.08, 140.81, 140.57, 139.59, 139.48, 132.93, 4 5 127.17, 126.70, 126.64, 126.43, 124.85, 122.61, 120.31, 120.25, 119.75, 119.36, 114.55, 54.84, 54.65, 39.92, 31.15, 29.23, 23.49, 22.06, 13.12. LCMS (APCI) calcd for C₄₅H₅₁NO₂ [M+H⁺] 638.4, 6 7 found 638.7. Elemental analysis calcd for C₄₅H₅₁NO₂: C, 84.73; H, 8.06; N, 2.20; O, 5.02. Found C, 8 84.88; H, 8.19; N, 2.04.

9

10 4.5.12 Sinthesis of 4-((9,9-dihexyl-9H-fluoren-2-yl)ethynyl)-N,N-bis(4-methoxyphenyl)aniline (VI)

A microwave reactor vessel was charged with compound 2 (300 mg, 0.728 mmol), compound 5 11 12 (288 mg, 0.874 mmol), CuI (4 mg, 0.036 mmol) and a mixture of 1/5 TEA/DMF (8 mL). The reaction mixture was stirred under a nitrogen atmosphere at rt for 10 minutes, then Pd(PPh₃)₂Cl₂ (10 13 mg, 0.015 mmol) and PPh₃ (76.58 mg, 0.292 mmol) were added. The resulting mixture was 14 15 submitted to a 100W power irradiation for 1h. Upon cooling, the mixture was diluted with diethyl ether and washed with water. The organic layer was dried over anhydrous Na₂SO₄ and the solvent 16 evaporated under vacuum. The crude product was purified by column chromatography on silica gel 17 (eluent petroleum ether/CH₂Cl₂ 1/1), to yield the pure product VI as a yellow wax-solid (yield 18 95%). ¹H NMR (400 MHz, Acetone- d_6): δ 7.82-7.78 (m, 2H), 7.57 (s, 1H), 7.49-7.45 (m, 2H), 7.36-19 20 7.34 (m, 4H), 7.12 (d, J = 9.0 Hz, 4H), 6.95 (d, J = 9.0 Hz, 4H), 6.79 (d, J = 8.8 Hz, 2H), 3.81 (s, 6H), 2.09-2.05 (m, 4H), 1.14-0.98 (m, 12H), 0.75 (t, 6H), 0.65-0.54 (m, 4H). ¹³C NMR (100 MHz, 21 Acetone- d_6) δ 156.71, 150.58, 148.95, 140.93, 140.34, 139.67, 139.65, 132.04, 130.08, 127.34, 22 127.29, 126.80, 125.31, 122.70, 122.06, 119.76, 119.54, 118.07, 114.72, 113.32, 89.85, 88.63, 23 54.86, 54.67, 39.82, 31.17, 29.22, 23.46, 22.09, 13.12. LCMS (APCI) calcd for C₄₇H₅₁NO₂ [M+H⁺] 24

1	662.40, found 662,7. Elemental analysis calcd for C ₄₇ H ₅₁ NO ₂ : C, 85.28; H, 7.77; N, 2.12; O, 4.38.
2	Found C, 85.49; H, 7.89; N, 2.15.
3	
4	CONFLICTS OF INTEREST
5	There are no conflicts of interest to declare.
6	
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Highlights

- Six biarylaminofluorene-based systems were synthesized and characterized.
- > Optically induced electron transfer pathway was investigated varying the length bridge connecting the redox centers.
- > Redox-controlled modulation of absorption and fluorescence was studied.
- \succ D-π-D⁺ showed interesting NIR absorption.

red

Authors' individual contributions

Agostina-Lina Capodilupo: Molecular design, writing and management of the work

Francesca Manni: Molecular synthesis

Antonio Cardone: Chemical characterization of organic compounds

Roberto Giannuzzi: Chemical oxidation experiments

Gianluca Accorsi: Photophysical characterization

Giuseppina Anna Corrente: Electrochemical characterization

Amerigo Beneduci: Electrochromic and electrofluorochromic investigations and interpretation and analysis of the data

Eduardo Fabiano: Computational investigation

Giuseppe Gigli: Critical revision of the work

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Declaration of interests

 \boxtimes The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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