Pergamon

SCIENCE DIRECT®

Tetrahedron 59 (2003) 2939–2945

TETRAHEDRON

Synthesis and photochemical behavior of donor–acceptor systems obtained from chloro-1,4-naphthoquinone attached to *trans*-aminostilbenes

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Received 17 September 2002; revised 14 January 2003; accepted 7 February 2003

Abstract—2-Chloro-1,4-naphthoquinone was covalently attached to six differently substituted and positional isomers of *trans*-aminostilbene, forming a novel donor–acceptor system (QST), in which a good fluorophore is bonded via an NH group to an active redox quencher. The new systems were characterized by FT-IR, ^{1}H NMR, HR-MS, UV–Vis and fluorescence spectroscopy. The redox state of the system QST/QH_2ST controls its photochemical properties. While the QST's behave as an 'auto-quenching system' and are non-fluorescent, the reduced hydroquinonic system (QH_2ST) affects appreciably the emission properties of the molecule.

1. Introduction

The ability to manipulate photochemical properties via redox states is of interest in biochemical and biophysical investigations, and such a system might find use as a probe for redox processes, and in studies of electron and energy transfer mechanisms. *trans*-Stilbene and its related substituted derivatives are a widely studied family of organic fluorophores. The unique structure of these molecules offers several advantages as potential photochrome probes in different organized media.[1] Their photochemical and photophysical behavior are well characterized[2–4] and both fluorescence emission and *trans–cis* photoisomerization reaction account for their excited state behavior in solution.[5] Double bond torsion proceeds from the lowest excited state ^{1}t* configuration through the twisted singlet intermediate ^{1}p* (phantom state), which has a very short lifetime and decays predominantly by photoisomerization. In the case of several substituted stilbenes, the intersystem crossing pathway (via the biradical twisted triplet state ^{3}p*) competes with singlet state fluorescence.[6]

Quinones are good electron acceptors and are known to be efficient quenchers of singlet state donor fluorescence of various fluorophores.[7–9] The current data are consistent with an electron transfer mechanism,[10,11] and the quenching efficiency is dependent on the redox potentials of the corresponding quinone–hydroquinone system. Such redox potentials in conjunction with fluorescence measurements are of utility in extra- and intracellular reduction states study.[12–15] Along similar lines, we deduced that direct covalent attachment of a quinone acceptor to the stilbene framework, will yield a novel type of donor–acceptor system in which an efficient fluorophore is bonded to an active redox quencher. The intrinsic fluorescence emission of the stilbene excited state will be strongly quenched by collisionless intramolecular electron transfer from the excited stilbene to the adjacent quinone acceptor, or by deactivation to a low-lying non-emissive charge-transfer state. It is expected however, that reduction of the stilbene-linked quinones to the corresponding stilbene-linked hydroquinones, will reduce or even remove this quenching effect. This dynamic system can be schematically represented as follows (Chart 1).

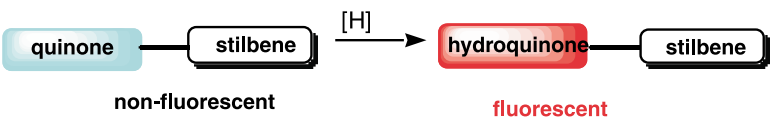

Chart 1. Fluorescent 'off/on' switch.

Keywords: quinone; hydroquinone; aminostilbene; fluorescence quenching; molecular switching system.
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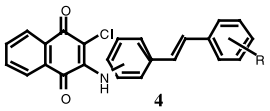
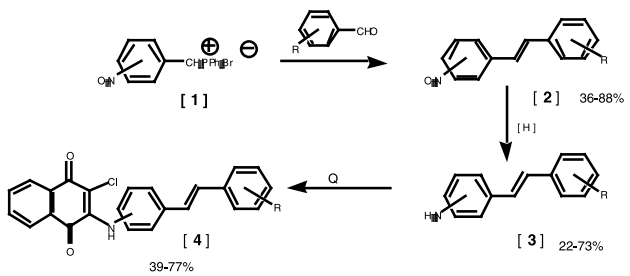
0040–4020/03/$ - see front matter
doi:10.1016/S0040-4020(03)00213-8



4

4	R	
a	H	*para*
b	H	*meta*
c	*para*-NH_2	*para*
d	*meta*-NH_2	*meta*
e	*para*-$N(CH_3)_2$	*para*
f	*para*-OCH_3	*para*

Chart 2. Chemical structure of QST compounds.



Q=2,3-dichloro-1,4-naphthoquinone

Scheme 1. Synthetic routes for *N*-quinonyl *trans*-aminostilbenes formation.

In the present paper we describe the synthesis and some photochemical properties of such novel donor–acceptor systems (QST's) in which chloronaphthoquinone (acceptor) is covalently attached, via an NH spacer, to various substituted *trans*-stilbenes at the *para*- or *meta*-positions (donors) (Chart 2). Chemical reduction of the *N*-quinonyl moiety could be achieved without any modification of the *trans*-stilbene moiety yielding the *N*-hydronaphthoquinone-stilbene systems (QH_2ST).

The photochemical behavior of these new stilbene derivatives, was also compared to that of the starting materials.

2. Results and discussion

2.1. Synthesis

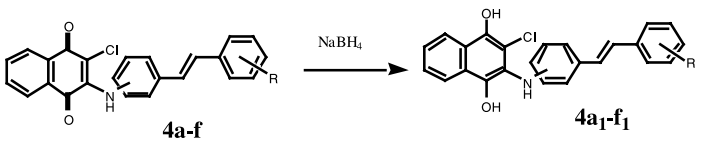
The various quinonostilbenes (QST's) were prepared by modification of known procedures (Scheme 1).[16–19]

The nitrostilbenes **2** were prepared by the Wittig reaction and reduced to the corresponding *trans*-aminostilbenes **3**. The mono-quinonostilbenes **4** (Chart 2) were obtained via 1,4-Michael type addition. The hydroquinonostilbenes $\mathbf{4a_1}$–$\mathbf{4f_1}$ (QH_2ST) were obtained by chemical reduction of **4a**–**4f** using $NaBH_4$ as a reducing agent (Scheme 2).

2.2. FT-IR, ^{1}H NMR and MS

In the IR spectra of the synthesized QST's, two typical strong quinonic carbonyl absorptions are observed between 1635 and 1670 cm^{-1}. The NH absorption appears around 3200 cm^{-1}, and multiple aromatic bands can be seen around 1600 cm^{-1}. In the ^{1}H NMR spectra of the QST's, four naphthalenic protons with different chemical shifts are observed, as expected from such non-symmetrical systems (Fig. 1). The NH protons of all QST's resonate as a broad singlet between 6.7 and 7.7 ppm. The vinylic protons appear as an AB quartet between 7.0 and 7.2 ppm with coupling constants of 12.0–16.0 Hz, which substantiate the *trans* non-symmetrical configuration of the stilbene system.

In the mass spectra, almost all the QST's conjugates gave an intense M^+ parent ion. In addition, all the compounds gave one or two fragments typical to quinonic stepwise decarbonylation process, e.g. $[M^+-CO]$ and $[M^+-2CO]$.



4a-f **$4a_1$-f_1**

4	R	
a	H	*para*
b	H	*meta*
c	*para*-NH_2	*para*
d	*meta*-NH_2	*meta*
e	*para*-$N(CH_3)_2$	*para*
f	*para*-OCH_3	*para*

4	R	
a1	H	*para*
b1	H	*meta*
c1	*para*-NH_2	*para*
d1	*meta*-NH_2	*meta*
e1	*para*-$N(CH_3)_2$	*para*
f1	*para*-OCH_3	*para*

Scheme 2. Formation of *N*-hydroquinonyl aminostilbenes $\mathbf{4a_1}$–$\mathbf{4f_1}$ upon the reduction of **4a**–**4f**.

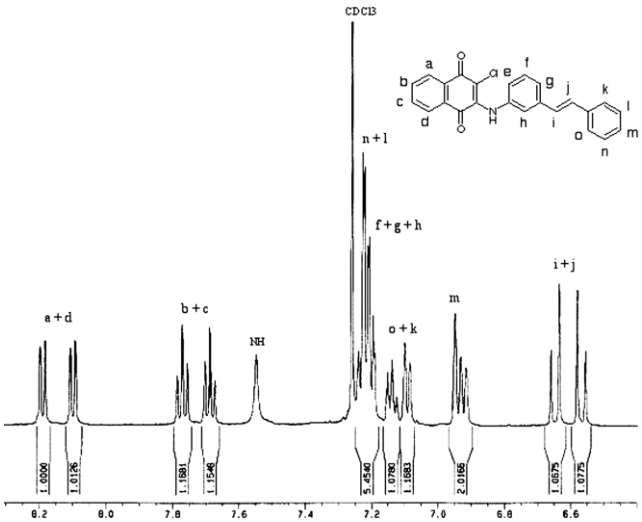


Figure 1. ^{1}H NMR spectrum of **4b** in $CDCl_3$.

Table 1. Absorption parameters for the series **4a**–**4f** in DMSO and for the starting aminostilbenes **3a**–**3f** in different solvents

Compound	Absorption maximum (λ_{max} (nm))	Molar absorptivity (log ϵ)
4a	281, 346, 493	4.16, 3.70, 3.34
4b	278, 490	4.62, 3.70
4c	284, 358, 539	4.29, 4.54, 3.78
4d	280, 488	4.70, 3.77
4e	282, 357, 537	4.15, 4.43, 3.62
4f	281, 340, 493	4.80, 3.98, 4.05
3a	318(sh), 336	4.49, 4.51
3b	300, 336(sh)	4.41
3c	336	4.44
3d	298, 335(sh)	–
3e	368	–
3f	350	–

2.3. Absorption spectra

The absorption parameters of QST series **4a**–**4f** in DMSO along with data from the literature[20–22] for the appropriate aminostilbenes **3a**–**3f** are reported in Table 1. The absorption spectra of **4a**–**4f** in DMSO solution are shown in Figure 2.

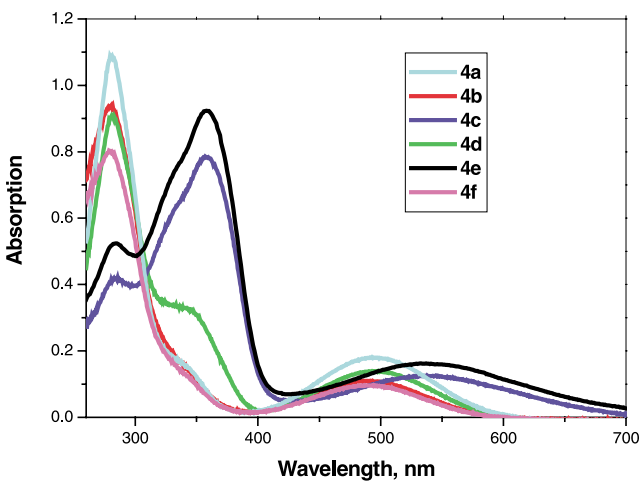


Figure 2. Absorption spectra of **4a**–**4f** in DMSO.

The absorption spectra of **4a**, **4b**, **4d** and **4e**, display an intense band having maxima near 280 nm and a shoulder of lower intensity between 340 and 358 nm. The 280 nm band is attributed to $\pi-\pi^*$ transitions of the quinonic moiety.[23] The stilbene absorption of QST's **4c**, **4e** and **4f** (344, 368, and 350 nm) are red shifted as compared to aminostilbenes **3c**, **3e**, and **3f** (358, 357 and 340 nm) (see Table 1), due to the increased π-delocalization of the chromophore, (the mesomeric effect).[24] An opposite effect was observed for the *meta* substituted QST's, **4b** and **4d**. The stilbene absorption (at 300 and 298 nm) is blue shifted in the QST's (278 and 280 nm), which cause overlapping with the quinonic transitions at 278–280 nm. This blue shift is probably due to increased steric interactions in the excited states of the *meta* and *meta*, *meta* compounds.

All six synthesized QST's (**4a**–**4f**) show the typical long wavelength amino-substituted quinonoid $\pi-\pi^*$ broad transition at 490–539 nm. Such absorption is typical of amino-substituted benzoquinones, naphthoquinones and anthraquinones.[25] On the basis of donor strength of the substituent, the *para*-amino-QST (**4c**) and the *para*-dimethylamino-QST (**4e**) are considerably red-shifted (539 and 537 nm, respectively) relative to the other QST's which absorb around 490 nm. The *meta*-amino-QST (**4d**) is blue shifted as well, compared to the *para*-amino derivatives. Such phenomena have already been observed in the series of amino substituted stilbenes and have been explained on molecular symmetry grounds.[26]

A different picture is obtained with the reduced QH_2ST molecules $\mathbf{4a_l}$–$\mathbf{4f_l}$ (Table 2, Figs. 3 and 4). First, the reduction of the quinonic compounds (QST's) to the

Table 2. Absorption parameters for the series $\mathbf{4a_l}$–$\mathbf{f_l}$ in DMSO

Compound	Absorption maximum (λ_{max} (nm))	Molar absorptivity (log ϵ)
$\mathbf{4a_l}$	360	3.94
$\mathbf{4b_l}$	367	4.28
$\mathbf{4c_l}$	327(sh), 384	4.33, 4.57
$\mathbf{4d_l}$	364	4.36
$\mathbf{4e_l}$	326(sh), 385	4.19, 4.44
$\mathbf{4f_l}$	372	4.55

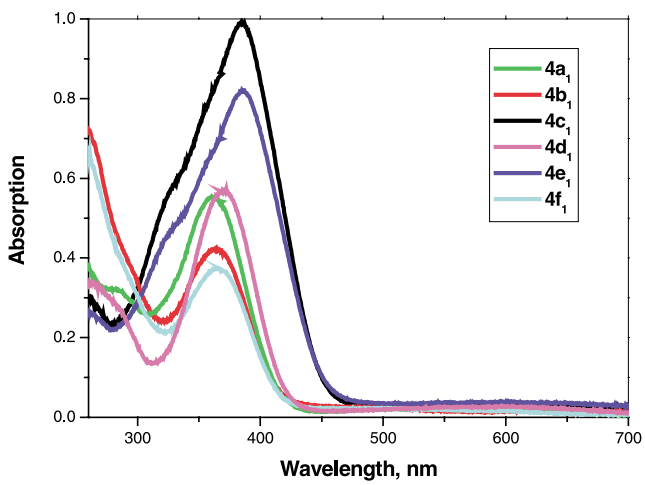


Figure 3. The absorption spectra of $\mathbf{4a_l}$–$\mathbf{f_l}$ in DMSO.

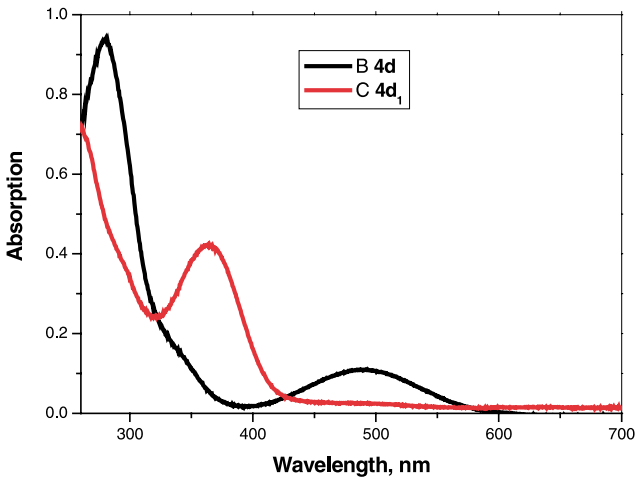


Figure 4. The absorption spectra of **4d** vs **4d$_l$** in DMSO.

switching system', where the emission and the absorption properties are controlled by the redox state of the quinonic moiety of the molecule.

The fluorescence excitation and emission maxima of **4a$_l$**–**4f$_l$**, in water or in DMSO solution, along with quantum yields (θ_f) and Stokes shifts ($\Delta\nu_{st}$) are summarized in Table 3 along with literature values[20–22] for the starting aminostilbenes. The Stokes shift values were estimated using the Berlman's method,[28] using the values of absorption and emission maxima.

The typical excitation/emission spectra of *N*-hydronaphthoquinonyl aminostilbene are shown in Figure 5.

The emission spectra of **4a$_l$**–**4f$_l$** are independent of excitation wavelength at room temperature, they are broad and display no vibronic structure in the solvents used. The

Table 3. Fluorescence parameters and quantum yields of the reduced QST's **4a$_l$**–**4f$_l$**, measured using quinine sulphate in 0.1 M H_2SO_4 as a standard along with data for starting aminostilbenes **3a**–**3f**

Compound	λ_{max}(ex) (nm)	λ_{max}(em) (nm)	Quantum yield θ_f	Stoke's shift (cm^{-1}) $\Delta\nu_{st}$	Fluorescence lifetime τ_1 (ns)	Fluorescence lifetime τ_2 (ns)
4a$_l$ (water)	324	445	0.007	5305	<0.5 (87.5%)	4.81 (12.5%)
4b$_l$ (DMSO)	338	478	0.062	6327	8.94 (100%)	–
4c$_l$ (water)	370	423	0.377	2401	1.73 (94.79%)	8.63 (5.21%)
4d$_l$ (DMSO)	330	465	0.021	5967	2.17 (23.1%)	8.31 (76.9%)
4e$_l$ (water)	331	435	0.521	2985	<0.5 (97.6%)	5.39 (2.4%)
4f$_l$ (DMSO)	340	436	0.160	3945	1.53 (64.7%)	7.75 (35.32%)
3a (ACN)	–	423	0.03	3127	~0.1	–
3b (ACN)	–	446	0.4	3906	11.7	–
3c (water)	–	414	0.04	6340	~0.3	–
3d (EtOH)	–	455	0.24	7873	9.5	–
3e (DMSO)	–	422	0.92	3476	1.18	–
3f (DMSO)	–	427	0.082	5151	0.099	–

hydroquinonic compounds (QH_2ST) is followed by complete disappearance of the long-wavelength absorbance (488–539 nm). The spectra of all these compounds consist of a single intense band between 360–385 nm. These absorption maxima are red shifted as compared to that of the appropriate QST's (e.g. Fig. 4) or to that of the starting aminostilbenes and resembles the absorption behavior of *N*-aryl substituted-*trans*-4-aminostilbenes.[27]

The largest shifts were observed for the pair 4-amino-QST-QH_2ST (**4c**–**4c$_l$**) and 4-*N*-dimethylamino-QST-QH_2ST (**4e**–**4e$_l$**) due to the enhanced mesomeric effects with the substituents.

2.4. Fluorescence spectroscopy

Auto-quenching of fluorescence in the QST series was clear cut. Thus, no fluorescence emission was observed for the synthesized series of *N*-naphthoquinonyl aminostilbenes (**4a**–**4f**) at room temperature, while their reduced *N*-hydronaphthoquinonyl aminostilbenes analogues (**4a$_l$**–**4f$_l$**) exhibit under the same conditions different degrees of fluorescence emission. This total quenching of the aminostilbene fluorescence in the QST molecule is attributed to the efficient electronic coupling between the quinonic acceptor and the stilbene donor, via amino bridge. Each QST/QH_2ST system can be considered as a 'molecular

fluorescence maxima of all the QH_2ST's are appreciably red-shifted relative to that of the starting aminostilbenes (Table 3). The reduction of the quinonic to the hydroquinonic compounds, introduces an *N*-aryl substituent to the aminostilbenes, which leads to a more planar ground-state geometry about the nitrogen atom ('amino conjugation effect').[29] This effect is observed in our case, despite the fact that the two *ortho* positions to the NH group are substituted (an hydroxy group on one side and a chlorine atom on the

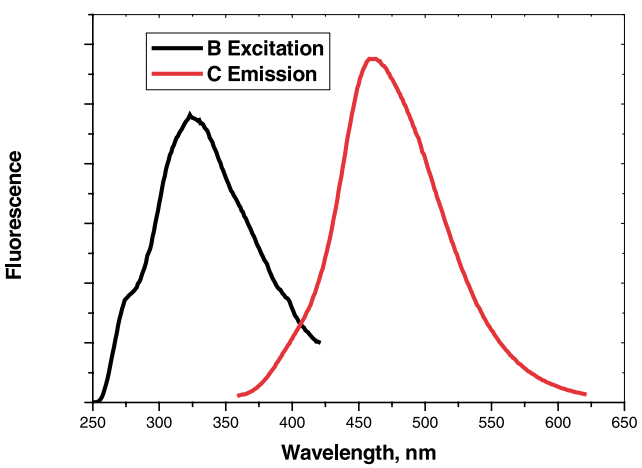


Figure 5. The excitation and emission spectra of **4f$_l$** in water at rt.

other side). Such a structure leads usually to less planar amine geometry and weaker orbital interactions between the *N*-aryl and the aminostilbene moieties.[27] The fact that we do observe considerable fluorescence emission in our QH_2ST's might reflect the influence of intramolecular hydrogen bond formation, which induces stronger orbital interactions between the two parts of the molecule.

Fluorescence quantum yields (θ_f) and the Stokes shifts determined at room temperature for the QH_2ST's **4a$_1$**–**4f$_1$**, show that non-radiative deactivation of excited state S_1, in which the *trans*–*cis* photoisomerization is the major process, dominates during the $S_1 \rightarrow S_0$ transition. The intersystem crossing pathway as a second non-radiative deactivation process, was not considered here. The intersystem crossing pathway competes with singlet state isomerization and fluorescence only in the case of the halogenated or nitro-substituted stilbenes.[30]

The fluorescence lifetimes of the QH_2ST's **4a$_1$**–**f$_1$** at room temperature are reported in Table 3. A typical fluorescence decay profile is shown in Figure 6.

In all cases, except **4b**, dual-exponentional decay was observed. Shortest decay times (0.5–2 ns) were observed for the *para*-substituted **4a**, **4c**, **4e** and **4f** as a major lifetime component, while the second long decay component was detected as minor. On the contrary, the *meta*-substituted compounds **4b** and **4d** display long decay times as a major component. The fluorescence lifetimes of **4a** and **4e** are very close to the values for the starting aminostilbenes, however, decay times for **4c** and **4f** are significantly longer than those of the starting aminostilbenes. The fluorescence lifetimes of the *meta*-substituted compounds **4b** and **4d** are much longer than those of the *para*-analogs, but still smaller than those of the starting *meta*-aminostilbenes.

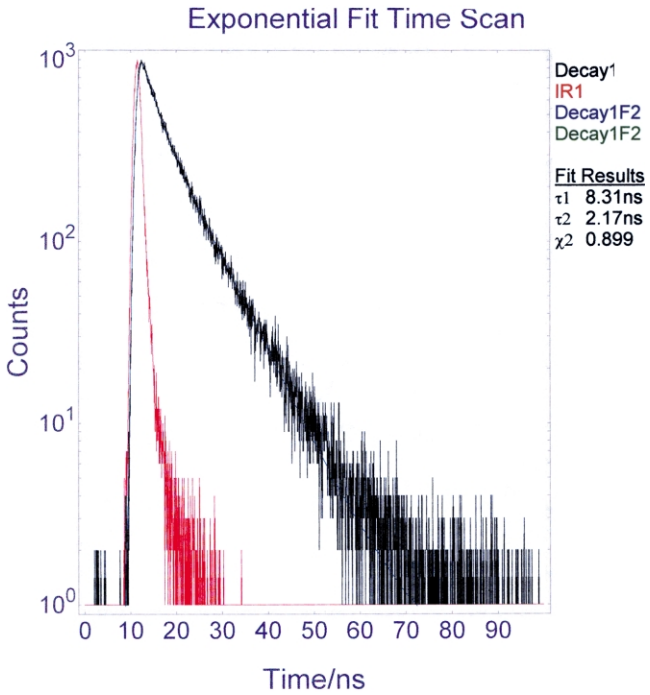


Figure 6. Time-resolved fluorescence decay profile of **4b** in DMSO. The experimental data was fitted after convolution with χ^2=0.9.

3. Concluding remarks

Introducing a chloro-naphthoquinone substituent into *trans*-aminostilbenes results in complete quenching of fluorescence. Upon reduction of the quinonic moiety to a hydroquinonic moiety strong fluorescence emission reappears. Using these systems it might be possible to manipulate photochemical properties via redox states and such a system might find use as probes for redox processes in biochemical and biophysical investigations. The *para*-disubstituted compounds (e.g. **4c$_1$**, **4e$_1$** and **4f$_1$**) show intensive fluorescence, thus are more promising in this respect than the *meta*-di-substituted compounds (e.g. **4b$_1$** and **4d$_1$**).

4. Experimental

4.1. Instruments and methods

IR spectra were recorded on a Nicolet 5ZDX FT-IR spectrometer. ^{1}H NMR data was obtained with Bruker Advance DMX 500 or Bruker Advance DPX 200 spectrometers. UV–Vis absorption spectra were recorded on a Hewlett–Packard UV–Vis 200HP diode array spectrophotometer using a 1 cm path length quartz cell. Fluorescence emission spectra were performed on a SLM Aminco-Bowman spectrofluorimeter with excitation near the absorption maximum of the stilbene moiety, using 8 nm spectral resolution for both excitation and emission. All fluorescence spectra are corrected and 10^{-6} M quinine sulphate in 0.1 M H_2SO_4 solution was used as an internal standard. Quinine sulphate was used as a standard for the fluorescence quantum yield determination with solvent refractive index correction. Fluorescence decays were measured at room temperature by means of an Edinburgh FL 920 spectrofluorimeter using a scatter solution to profile the instrument response function. The goodness of nonlinear least-squares fit was judged by reduced χ^2 value ($<$1.3 in all cases). All spectroscopic measurements were performed on solutions that were purged with dry N_2 for about 30 min. The identity of all compounds was established by HRMS (CI in methane), which were obtained using a Finnigan 4020 quadropole spectrometer. Melting points were determined using a Thomas–Hoover capillary apparatus and are uncorrected.

4.2. Chemicals

All chemicals and reagents were of analytical grade. Solvents used in the synthetic procedures were of reagent grade, further purified by accepted procedures. For all the fluorimetric experiments, spectrophotometric grade DMSO, (Aldrich) was used. $NaBH_4$ was obtained from Aldrich and used as the reducing agent.

The 4 and 3-nitrobenzyltriphenylphosphonium bromides **1** were prepared according to known procedures.[31,32] The nitrostilbenes **2** were obtained via Wittig or Perkin reactions.[32–37] The aminostilbenes 3 were prepared by chemical reduction of nitrostilbenes **2**.[35,37–40]

4.2.1. Syntheses. *E*-4-*N*-(3-chloro-1,4-naphthoquinon-2-yl)-aminostilbene [4a]. A mixture of *E*-4-aminostilbene

[**3a**] (0.9 g, 4.6 mmol) and 2,3-dichloro-1,4-naphthoquinone (2.1 g, 9.3 mmol) in 50 mL EtOH was stirred for 24 h at rt. The solvent was evaporated under reduced pressure to afford a red crude solid. The product was isolated by chromathography on silica eluting with a mixture of petrol ether (60–80)/DCM (1:9). Yield (0.85 g, 48%) red solid, mp 172–175°C; ν_{max} (KBr, cm^{-1}) 1615(CH), 1642 and 1689(quinonic C═O), 3267(NH); λ_{max} (EtOH, nm, log ε) 488(3.58), 280(4.40), 236(4.28), 206(4.50); δ_H (200 MHz, $CDCl_3$) 7.21 (1H, d, J=16 Hz, stilbene vinyl), 7.28 (1H, d, J=16 Hz, stilbene vinyl), 7.32–7.47 (3H, m, phenyl), 7.56 (1H, dd, J_{ortho}=8.1, J_{meta}=1.8 Hz, phenyl), 7.63 (1H, d, J=8.8 Hz, phenyl), 7.68 (1H, td, J_{ortho}=7.7, J_{meta}=1.3 Hz, naphthoquinone), 7.76 (1H, td, J_{ortho}=7.5, J_{meta}=1.2 Hz, naphthoquinone), 8.1 (1H, dd, J_{ortho}=7.7, J_{meta}=0.85 Hz, naphthoquinone), 8.25 (1H, dd, J_{ortho}=7.7, J_{meta}=0.85 Hz, naphthoquinone). HR-MS (CI in CH_4) (*m*/*z*): 385.0869 (M^+, calcd 385.0870 for $C_{24}H_{16}ClNO_2$), 297($MH_2^+-Cl-2CO$), 195(M^+-naphthoquinone).

4.2.2. *E*-3-*N*-(3-Chloro-1,4-naphthoquinon-2-yl)-aminostilbene [4b]. A mixture of *E*-3-aminostilbene [**3b**] (0.39 g, 2 mmol) and 2,3-dichloro-1,4-naphthoquinone (0.9 g, 4 mmol) in 50 mL EtOH was stirred for 24 h at rt. The solvent was evaporated under reduced pressure to afford red crude solid. The product was isolated by chromathography on silica eluting with DCM and recrystallized from EtOH. Yield (0.3 g, 39%) red small crystals, mp 100–102 °C; ν_{max} (KBr, cm^{-1}) 1568(CH), 1642 and 1682(quinonic C═O), 3227(NH); λ_{max} (EtOH, nm, log ε) 488(3.84), 278(4.64), 234(4.34), 206(4.50); δ_H(500 MHz, $CDCl_3$) 6.57 (1H, d, J=12.2 Hz, stilbene vinyl), 6.64 (1H, d, J=12.2 Hz, stilbene vinyl), 6.95 (1H, s, stilbene ring), 7.09 (1H, d, J=7.6 Hz, stilbene ring), 7.22 (6H, m, stilbene ring), 7.54 (1H, s, NH), 7.68 (1H, td, J_{ortho}=7.7, J_{meta}=1.3 Hz, naphthoquinone), 7.76 (1H, td, J_{ortho}=7.5, J_{meta}=1.2 Hz, naphthoquinone), 8.1 (1H, dd, J_{ortho}=7.7, J_{meta}=0.85 Hz, naphthoquinone), 8.2 (1H, dd, J_{ortho}=7.7, J_{meta}=0.85 Hz, naphthoquinone). HR-MS (CI in CH_4) (*m*/*z*): 385.0869 (M^+, calcd 385.0870 for $C_{24}H_{16}ClNO_2$) 297($MH_2^+-Cl-2CO$), 195(M^+-naphthoquinone).

4.2.3. *E*-4-*N*-(3-Chloro-1,4-naphthoquinon-2-yl) -amino-4′-aminostilbene [4c]. A mixture of 2,3-dichloro-1,4-naphthoquinone (0.86 g, 3.8 mmol) and *E*-4,4′-diaminostilbene [**3c**] (0.4 g, 1.9 mmol) in 30 mL EtOH was stirred for 24 h at rt. The solvent was evaporated under reduced pressure to afford blue crude solid. The product was isolated by chromathography on silica eluting with DCM and recrystallized from EtOH. Yield (0.35 g, 46%) small purple crystals, mp 192 °C; ν_{max} (KBr, cm^{-1}) 1602(CH), 1642 and 1676 (quinonic C═O), 3234 (NH, NH_2); λ_{max} (EtOH, nm, log ε) 488(3.16), 334(3.90), 280(4.33), 208(4.45); δ_H(500 MHz, $CDCl_3$) 6.66 (2H, d, J=8.4 Hz, stilbene ring), 6.88 (1H, d, J=16.3 Hz, stilbene vinyl), 7.01 (1H, d, J=16.2 Hz, stilbene vinyl), 7.02 (2H, d, J=8.3 Hz, stilbene ring), 7.32 (2H, d, J=8.4 Hz, stilbene ring), 7.43 (2H, d, J=8.4 Hz, stilbene ring), 7.68 (1H, td, J_{ortho}=7.55, J_{meta}=1.2 Hz, naphthoquinone), 7.76 (1H, td, J_{ortho}=7.50, J_{meta}=1.3 Hz, naphthoquinone), 8.11 (1H, dd, J_{ortho}=7.65, J_{meta}=1.0 Hz, naphthoquinone), 8.18 (1H, dd, J_{ortho}=7.60, J_{meta}=1.0 Hz, naphthoquinone). HR-MS (CI in methane) (*m*/*z*): 400.0978 (M^+, calcd 400.0979 for $C_{24}H_{17}ClN_2O_2$), 366(M^+-Cl), 298($M^+-Cl-2CO-NH_2$).

4.2.4. *E*-3-*N*-(3-Chloro-1,4-naphthoquinon-2-yl)-amino-3′-aminostilbene [4d]. A mixture of *E*-3,3′-diaminostilbene [**3d**] (1.26 g, 6 mmol) and 2,3-dichloro-1,4-naphthoquinone (1.36 g, 6 mmol) in 50 mL EtOH was stirred for 24 h at rt. The solvent was evaporated under reduced pressure to afford red crude solid. The product was isolated by chromathographic column on silica gel eluting with DCM and recrystallized from EtOH. Yield (1.45 g, 60%) red crystals, mp 85–90 °C; ν_{max} (KBr, cm^{-1}) 1561(CH), 1634 and 1682(quinonic C═O), 3227(NH), 3422(NH_2); λ_{max} (EtOH, nm, log ε) 488(4.46), 278(4.38), 222(4.25), 206(4.32); δ_H(500 MHz, $CDCl_3$) 6.46 (1H, dd, J_{ortho}=7.9, J_{meta}=1.5 Hz, stilbene ring), 6.51 (1H, d, J=12.2 Hz, stilbene vinyl), 6.56 (1H, s, stilbene ring), 6.57, d, J=12.2 Hz, stilbene vinyl), 6.62 (1H, d, J=7.6 Hz, stilbene ring), 6.98 (1H, t, J=7.7, stilbene ring), 6.99 (1H, s, stilbene ring), 6.92 (1H, d, J=7.9 Hz, stilbene ring), 7.11 (1H, d, J=7.8 Hz, stilbene ring), 7.21 (1H, t, J=7.8, stilbene ring), 7.68 (1H, td, J_{ortho}=7.6, J_{meta}=1.3 Hz, naphthoquinone), 7.77 (1H, td, J_{ortho}=7.6, J_{meta}=1.3 Hz, naphthoquinone), 8.10 (1H, dd, J_{ortho}=7.65, J_{meta}=0.8 Hz, naphthoquinone), 8.18 (1H, dd, J_{ortho}=7.7, J_{meta}=0.85 Hz, naphthoquinone). HR-MS (CI in methane) (*m*/*z*): 400.0978 (M^+, calcd 400.0979 for $C_{24}H_{17}ClN_2O_2$), 366(M^+-Cl), 298($M^+-Cl-2CO-NH_2$), 193(2-chloro-1,4-naphthoquinone).

4.2.5. *E*-4-*N*-(3-Chloro-1,4-naphthoquinon-2-yl)-amino-4′-*N*,*N*-dimethylaminostilbene [4e]. A mixture of *E*-4-*N*-dimethylamino-4′-aminostilbene [**3e**] (0.4 g, 1.7 mmol) and 2,3-dichloro-1,4-naphthoquinone (0.56 g, 2.5 mmol) in 50 mL 95% ethanol was stirred for 24 h at rt. The solvent was evaporated under reduced pressure. The product was isolated by chromathography on silica eluting with the mixture of ethyl acetate/DCM (1:9) and recrystallized from DMSO/water. Yield (0.56 g, 77%) purple crystals, mp 195–200 °C; ν_{max} (KBr, cm^{-1}) 2965(NH), 1682 and 1635 (quinonic C═O); λ_{max} (EtOH, nm, log ϵ) 512(3.56), 342(4.41), 282(4.34), 206(4.70); δ_H(500 MHz, DMSO-d6) 2.40 (6H, s, Me_2N), 6.71 (1H, d, J=8.8 Hz, stilbene ring), 6.93 (1H, d, J=16.3 Hz, stilbene vinyl), 7.08 (2H, dd, J_{ortho}=16.2, J_{meta}=8.3 Hz, stilbene ring and vinyl part), 7.43 (2H, dd, J_{ortho}=8.7, J_{meta}=8.4 Hz, stilbene ring), 7.80–7.85 (2H, m, J_{ortho}=7.5, J_{meta}=1.1, naphthoquinone), 8.02 (2H, d, J=8.2 Hz, naphthoquinone). HR-MS (CI in methane) (*m*/*z*): 430(MH_2^+), 428.1324 (M^+, calcd 428.1292 for $C_{26}H_{21}ClN_2O_2$), 400 ($MH_2^+-(CH_3)_2$), 366 ($MH_2^+-Cl-(CH_3)_2$), 319($MH_2^+-CO-Cl-N(CH_3)_2$).

4.2.6. *E*-4-*N*-(3-Chloro-1,4-naphthoquinon-2-yl)-amino-4′-methoxystilbene [4f]. A mixture of *E*-4-methoxy-4′-aminostilbene [**3f**] (0.6 g, 2.6 mmol) and 2,3-dichloro-1,4-naphthoquinone (1.82 g, 8 mmol) in 70 mL 95% EtOH was stirred overnight at rt. The solvent was evaporated under reduced pressure to afford purple crude solid. The product was isolated by chromatography on silica eluting with DCM and recrystallized from 95% EtOH. Yield (0.6 g, 55%) small purple crystals, mp 184 °C; ν_{max} (KBr, cm^{-1}) 1615(CH), 1635 and 1682 (quinonic C═O), 3207(NH); λ_{max} (DCM, nm, log ε) 482(3.77), 332(4.60), 234(4.35), 220(4.02); δ_H(500 MHz, DMSO-d6) 3.2 (3H, s, OMe), 6.93

(2H, d, J=8.6 Hz, stilbene ring), 7.12 (4H, m, stilbene ring and vinyl), 7.50 (4H, m, stilbene ring), 7.8 (2H, t, J=7.3, naphthoquinone), 8.01 (2H, d, J=7.6 Hz, naphthoquinone). HR-MS (CI in methane) (m/z): 385.0903 (M^+-OCH_3, calcd 385.0890 for $C_{25}H_{18}ClNO_3$), 297($M^+-OCH_3-Cl-2CO$).

4.2.7. *E*-3-Bis-*N*-(3-chloro-1,4-naphthoquinone-2-yl)-aminostilbene [4g]. A mixture of *E*-3,3′-diaminostilbene [**3d**] (0.45 g, 2.14 mmol), K_2CO_3 (0.28 g, 2 mmol) and 2,3-dichloro-1,4-naphthoquinone (1.93 g, 8.5 mmol) in 75 mL 95% EtOH was stirred for 48 h at rt. The solvent was evaporated under reduced pressure to afford red crude solid. The product was isolated by chromathography on silica (eluant: DCM) and recrystallized from EtOH. Yield (0.65 g, 52%) red small crystals, mp 165 °C; ν_{max} (KBr, cm^{-1}) 1595(CH), 1642 and 1696(quinonic C=O), 3234(NH); λ_{max} (EtOH, nm, log ε) 488(3.85), 278(4.67), 206(4.70); δ_H(500 MHz, $CDCl_3$) 6.62 (2H, s, stilbene vinyl), 6.92 (2H, d, J=7.7 Hz, stilbene ring), 7.0 (2H, d, J=7.7 Hz, stilbene ring), 7.04 (2H, s, stilbene ring), 7.16 (2H, t, J=7.8, stilbene ring), 7.75 (2H, td, J_{ortho}=7.5, J_{meta}=1.1 Hz, naphthoquinone), 7.80 (2H, td, J_{ortho}=7.4, J_{meta}=1.1 Hz, naphthoquinone), 7.90 (2H, dd, J_{ortho}=7.55, J_{meta}=1.2 Hz, naphthoquinone), 7.96 (2H, dd, J_{ortho}=7.5, J_{meta}=1.3 Hz, naphthoquinone). HR-MS (CI in methane) (m/z): 591.0878 (M^+, calcd 590.0800 for $C_{34}H_{20}Cl_2N_2O_4$), 400(M^+-naphthoquinone), 365(M^+-naphthoquinone$-$Cl), 193($M^+-2\times$naphthoquinone).

Acknowledgements

This research was supported by the Israel Science Foundation founded by the Academy of Science and Humanities and German-Israel James Frank Program on Laser-Matter Interaction. We wish to thank Ms Ethel Solomon for skilled technical help and A. Novoselsky for his advice on NMR spectroscopy. We greatly appreciate Dr S. Kolusheva for obtaining the fluorescence lifetime data and helpful discussions.

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