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Chromenes involving a two-photon absorbing moiety: photochromism *via* intramolecular resonance energy transfer

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New derivatives involving the photochromic 2*H*-benzo[*h*]chromene moieties covalently linked to the 2,7-bis(carbazolyl)fluorene-derived two-photon absorbing moiety were designed to enable the possibility of resonance energy transfer from the fluorene donor to the photochromic acceptor. The longest wavelength absorption of the photochromic acceptors overlaps with the fluorescence band of the two-photon absorbing donor and the distance between the both moieties is about 5–7 Å. Rapid coloration of colorless solutions was observed upon one- and two-photon absorption.

Introduction

Photochromism, defined as a reversible transformation of chemical species, induced in one or both directions by electromagnetic radiation[1] attracts considerable interest owing to the potential use of this phenomenon in various applications. Among such applications, the development of optical data storage materials,[2] optical limiting,[3] and manipulating supramolecular self-assemblies[4] should be mentioned. Using two-photon absorption (2PA) instead of one-photon absorption for inducing photochromic transformations offers further advantages and opens new possibilities in data recording and biomedical applications.[5]

Most of the known organic photochromes possess very small 2PA cross section values and the multiphoton-induced photochromic phenomena can be observed in solid state[6] or in polymer matrix containing 1.3 M of a photochromic material in the presence of gold nanoparticles.[7] Rendering large 2PA cross sections by chemical modification of the photochrome structure, such as attaching a molecule with the large 2PA cross section, is difficult to achieve, as the resulting molecule may exhibit weaker photochromic response or even lose the photochromic properties.[8] Porphyrin–perinaphthothioindigo and azo conjugates can be mentioned as a successful realization of this approach,[9,10] for a recent review see.[11]

An alternative approach involves resonance energy transfer (RET) from a 2PA fluorophore as a donor to a photochrome as an acceptor. Previously, we demonstrated that a two-component mixture of a fluorophore and a spiroxazine-derived photochrome absorbs two photons and exhibits RET.[12] A two-fold enhancement in the rate of the photochromic conversion of a diarylethene-derived photochrome in the presence of 2-photon absorbing fluorenes was also demonstrated.[13]

Because of the strong dependence of RET efficiency on donor–acceptor separation, effective RET between separate molecules requires high concentrations of the components and is best suitable for aggregates or polymers.[14] This concentration requirement can be removed when the acceptor and donor are chemically linked. Several derivatives involving both a photochromic and a fluorescent moiety have been reported, targeting fluorescence switching using the RET phenomenon. In this case, however, the colored (open) forms of the photochromes played the role of energy donors, see for instance.[15] Diarylethenes were demonstrated to be the most suitable candidates as 2PA switching molecules so far, although their direct conjugation with the 2PA moiety can lead to relatively low 2PA cross section values.[16]

Here we report on the synthesis of a series of new bifunctional molecules involving the 2,7-bis(carbazolyl)fluorene-derived 2PA moiety covalently linked by the $(CH_2)_3$ bridge to the chromene-derived photochromic moiety (**1a–3a**) along with the model derivatives lacking the 2PA fragment (**1b–3b**) and give an account of their spectroscopic behavior in solution.

Results and discussion

The structures of 2*H*-benzo[*h*]chromene (2*H*-naphtho[1,2-*b*]pyran) derivatives **1–3** and synthetic routes toward them are shown

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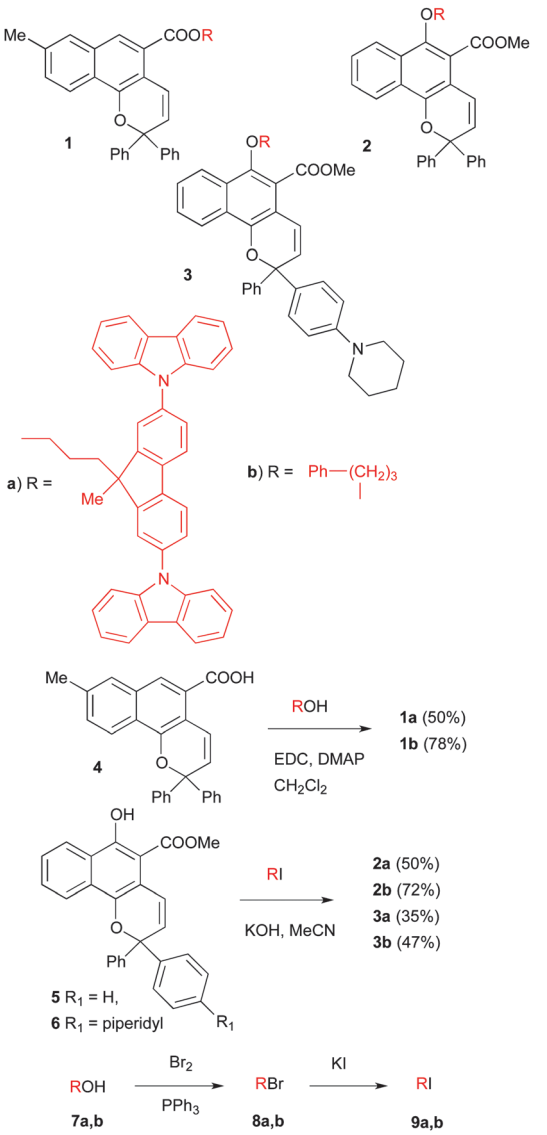
in Scheme 1. These derivatives were designed so that the longest wavelength absorption of the photochromic moiety overlaps with the fluorescence band of 9,9′-(9-(3-hydroxypropyl)-9-methyl-9*H*-fluorene-2,7-diyl)bis-9*H*-carbazole, and the distance between the photochromic and the 2PA moieties is about 5–6 Å to provide efficient RET and to exclude the possibility of through-bond and through-space intermolecular electronic interaction (This distance is calculated from the B3LYP/6-31G(d) geometry optimization. A detailed account of DFT calculations on derivatives **1–3** will be published elsewhere). At such distance between the donor and the acceptor moieties, both Förster- and Dexter-types of RET may be enabled.[17]

The structure variation **2** *vs.* **1** provides a shorter distance between the two moieties, whereas the variation **3** *vs.* **2** should give rise to a red shift in absorption of the respective colored forms owing to the presence of the amino group in the *para*-position of one of the phenyl groups.



Scheme 1 Derivatives **1–3** with the 2PA moiety (a-series) and model compound (b-series) and their synthesis.

Fluorene derivative **7a**[18] and the respective bromide **8a** and iodide **9a** (Scheme 1) were used for the modifications of the photochromic units **4**,[19] **5**[20] and **6** (prepared by analogy to ref. 20) owing to the high fluorescence quantum yield and relatively large 2PA cross section of the respective 2,7-bis(amino)fluorene derivatives.[21] The synthetic routes toward **1–3** are shown in Scheme 1. These compounds were purified by column chromatography and characterized by the NMR and HRM spectra. The best yields of derivatives **2** and **3** were achieved using iodides **9a,b**.

Derivative **1a** crystallizes out of acetonitrile solution as colorless crystals of two different shapes. The X-ray analysis showed that the rectangular prisms involve one molecule of acetonitrile per molecule of **1a** (Fig. 1), while the hexagonal prisms are solvent free.

The molecular geometry of **1a** in the crystals of both types is very similar and is characterized by the 'unfolded' conformation with the distance between the photochromic and 2PA moiety of about 6.9 Å, in contrast to the 'folded' configuration produced by the geometry optimization. There are several short intermolecular distances in the crystal lattice in both types of crystals that may constrain the molecule in this conformation.

The longest wavelength absorption bands of derivatives **1–3**, **a** – series in methylene chloride are observed as shoulders between 370 (**2**, **3**) and 380 nm (**1**), (ε about 10 000 M^{-1} cm^{-1}) on the strong absorption bands of the fluorene moiety (340 nm, ε about 80 000 M^{-1} cm^{-1}), overlapping well with the fluorescence band of **7a** (Fig. 2).

The absorption spectrum of **1a** represents an exact sum of the spectra of **1b** and **7a** indicating the absence of electronic interaction between the photochromic and 2PA moieties. Minor deviations in the absorption band positions and shapes in the spectra of **2a** and **3a** may indicate the presence of weak through-space interaction between the two functional moieties. No concentration dependence of the absorption spectra within the range of 10^{-3}–10^{-6} M was observed.

Whereas the dicarbazolyl fluorene precursor **7a** is strongly fluorescent (the quantum yield *ca.* 80%), derivative **1a** exhibits

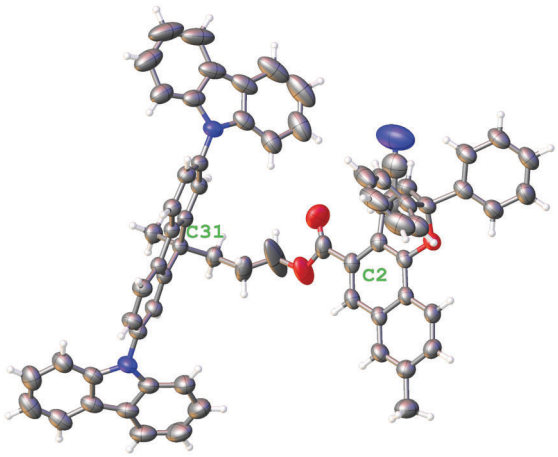


Fig. 1 ORTEP representation of the molecular structure of **1a** with one molecule of acetonitrile (thermal ellipsoids are presented at 50% of probability). C2–C31 distance is 6.923 Å.

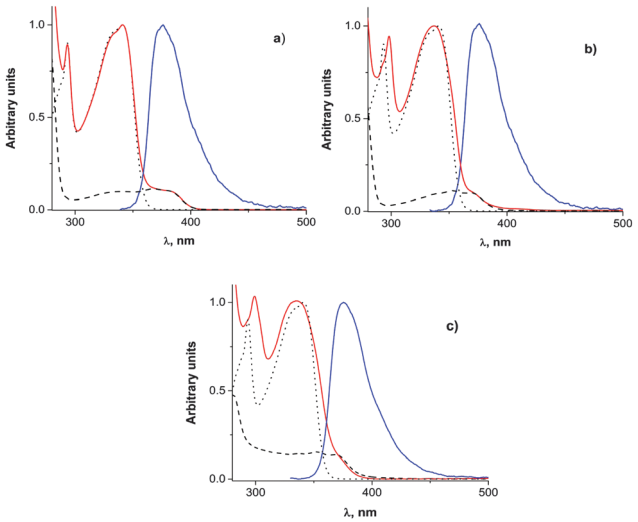


Fig. 2 Normalized absorption spectra in methylene chloride at 2×10^{-5} M: (a) **1**; (b) **2**; (c) **3**. Red: **a** – series; dashed: **b** – series; dotted: **7a**; blue: normalized fluorescence of **7a** (λ_{ex} = 330 nm).

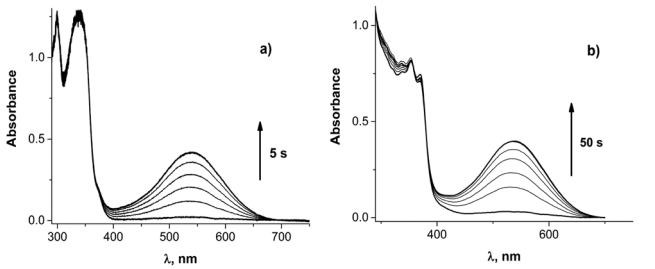


Fig. 3 Irradiation in toluene at 330 nm; (a) **3a** (1.2×10^{-5} M); (b) **3b** (10^{-4} M).

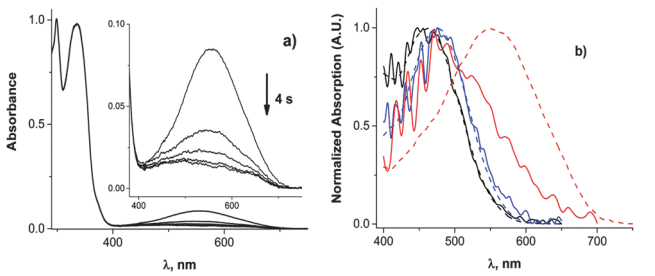


Fig. 4 (a) Thermal discoloration of **3a** irradiated at 330 nm in methylene chloride; (b) UV-Vis absorption spectra of **1a** (black), **2a** (blue) and **3a** (red) irradiated at 620 nm (solid lines) and 330 nm (dashed lines) in methylene chloride.

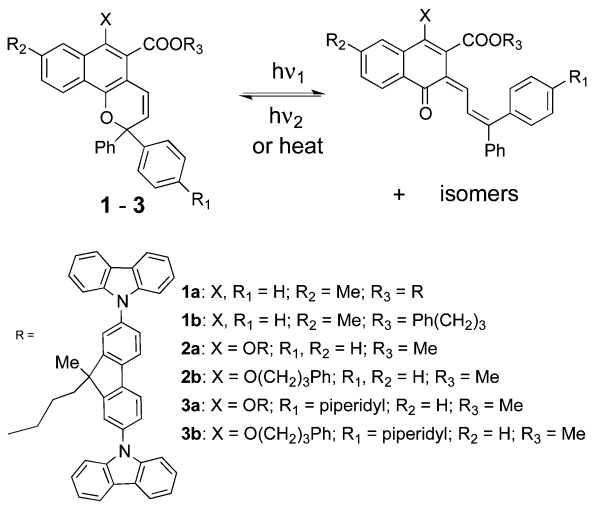
only weak fluorescence (the quantum yield *ca.* 1%) at about 380 nm and derivatives **2a** and **3a** are practically non-fluorescent. Such strong fluorescence quenching may indicate the occurrence of the efficient RET process. Irradiation of solutions of all six derivatives at 315, 330 or 350 nm (1PA) brings about rapid coloration owing to the formation of the colored open forms of the photochromes as a mixture of isomers (Scheme 2 and Fig. 3), yellow-orange for **1** and **2** and violet for **3**. A hypsochromic shift of the colored forms generated at 330 nm from **3a** is observed (Fig. 4a) during thermal discoloration owing to the different stabilities of the colored form isomers. Only derivatives **1a–3a** undergo coloration upon laser irradiation at 620 nm (2PA) (Fig. 4b), while derivatives **1b–3b** do not under the same conditions (Table 1).

Increasing polarity of the solvent (methylene chloride *vs.* toluene) brings about small shifts in the position of the absorption band maxima of the colored forms. The species generated by irradiation of **1a** and **2a** at 315, 330, 350 (1PA) and 620 (2PA) nm show similar absorption spectra (Fig. 4b).

The exception is **3a:** irradiation at 315 nm gives rise to a very broad absorption band covering all visible range red shifted by 16 nm in methylene chloride compared to toluene. The spectrum of femtosecond pulse at irradiation 620 nm overlaps with the absorption of the colored isomers and gives rise to the band shape distortion owing to photo-discoloration of the longer wavelength absorbing isomers (Fig. 4b). The color fading observed for this derivative is very rapid: the half-life time $t_{1/2}$ in methylene chloride is just 2 seconds (Table 1).

The half-life times of other derivatives vary in a non-systematic way and the variations can stem from steric rather than from the electronic factors. This phenomenon was observed also in the case of other chromene derivatives.[22]

Repeating of the coloration/discoloration cycles on derivatives **1–3** for 5–8 times did not reveal any noticeable fatigue features.



Scheme 2 Photochromism of derivatives **1–3**.

Table 1 Absorption maxima and the half-life times of the colored open isomers generated from **1–3** at 330 nm (1PA) and 620 nm (2PA)

Entry	$\lambda_{max}{}^{a}$ (nm)	$t_{1/2}{}^{a}$ (s)	$\lambda_{max}{}^{b}$ (nm)	$t_{1/2}{}^{b}$ (s)
1a	462	17	464 (465)[c]	35
1b	475	77	462	41
2a	472	77	475 (475)[c]	173
2b	475	178	478	173
3a	540	43	556 (480)[c]	2
3b	544	46	550	23

[a] In toluene. [b] In methylene chloride. [c] Irradiated at 620 nm.

Derivatives **1b–3b** do not exhibit coloration under 620 nm laser irradiation. A more detailed quantitative optical characterization of these compounds, including nonlinear properties, is currently under way.

Conclusions

The proposed synthetic protocol can be used to further optimize both the 2PA and photochromic moieties, as the non-conjugative tethering of the relatively bulky 2PA moiety to the photochromic 2*H*-benzo[*h*]chromenes (derivatives **1a–3a**) does not negatively affect their behavior as photochromic materials as compared to the derivatives **1b–3b**. All three derivatives **1a–3a** undergo coloration under femtosecond laser irradiation at 620 nm and quenching of fluorescence from the 2PA moiety corroborates the occurrence of the efficient RET process, whose exact nature still has to be established.

Experimental

Materials and measurements

The ^{1}H NMR spectra were recorded on a Brucker AC 250 spectrometer. Proton chemical shifts are reported in ppm downfield from tetramethylsilane. The elemental analyses and HRMS (Electrospray ionization) were made by the Microanalytical Center of Aix-Marseille Université. The UV-Vis absorption spectra were recorded with an Ocean Optics USB 4000 spectrometer for solutions with concentration of 1.5×10^{-5} M (derivatives **1a–3a** and **7a**) and 10^{-4} M (derivatives **1b–3b**). The fluorescence spectra were recorded with Ocean Optics USB +2000 spectrometer.

Single crystals of **1a** were grown from acetonitrile. X-ray crystallography data were collected on a Bruker-Nonius KappaCCD diffractometer with CCD detector using MoK_α radiation (λ = 0.71073 Å). Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre: **1a** involving one acetonitrile molecule: CCDC 1033558; solvent-free crystals: CCDC 1033559.

Irradiation of derivatives **1–3** in solution was done using LED sources LUMOS 43 (Atlas Photonics) at 315, 330, 350, 450 and 505 nm.

Two-photon experiments with derivatives **1a–3a** were done using an excite-probe method with a commercially available Ti:Sapphire amplified laser system (Coherent Legend Elite Duo HE +) producing 12 mJ, ~40 fs (FWHM) pulses at a 1 kHz repetition rate which pumps an optical parametric amplifier (TOPAS-HE) to produce the 1240 nm wavelength. A 3 mm BBO cut at 30.5° was used to generate second harmonic at 620 nm for two-photon excitation, and the residual fundamental radiation was blocked by a short pass filter at 1100 nm. The 620 nm excitation beam was focused to a spot size ~450 μm ($HW1/e^2M$) at the sample. A continuous white light probe beam, derived from a Deuterium lamp (Ocean Optics USB-DT), was focused to a beam radius of ~250 μm and overlapped with the excite beam in the sample. Samples of **1a**, **2a** and **3a** in methylene chloride (~3 mM) were irradiated in a 1 mm path length quartz cuvette. The pulses energy of 620 nm excitation was 30 μJ for **1a** and **2a**, and 50 μJ for **3a**. The optical density changes were recorded using an Ocean Optics HR4000 spectrometer to monitor the transmission of the white light.

Syntheses

Methyl 6-hydroxy-2-phenyl-2-[4-(1-piperidinyl)phenyl]-2*H*-benzo[*h*]chromene-5-carboxylate (6). A mixture of 1-phenyl-1-[4-(1-piperidinyl)phenyl]-2-propyn-1-ol (0.58 g, 2 mmol), methyl 1,4-dihydroxynaphthalene-2-carboxylate (0.43 g, 2 mmol), *p*-toluenesulfonic acid monohydrate (0.03 g, 0.2 mmol) and silica gel 60 (1 g) was ground in a mortar for 10 min at room temperature. The mixture was left to stand for 1 h. The reaction mixture was suspended in toluene (100 ml) and the insoluble part was filtered off. The filtrate was washed with 10% $NaHCO_3$ water solution (100 ml) and extracted with toluene (2 × 200 ml). The extract was washed with water (3 × 100 ml) and dried over $MgSO_4$. All volatiles were removed in vacuum and the product was purified by column chromatography on silica gel with CH_2Cl_2/Hex (2 : 1). After crystallization from MeOH, 0.63 g (65%) of the product **6** was obtained as beige powder with m.p. 146–148 °C. ^{1}H NMR ($CDCl_3$): 1.54 (2H, m, $C_5H_{10}N$); 1.70 (4H, m, $C_5H_{10}N$); 3.13 (4H, t, J = 5.6 Hz, $C_5H_{10}N$); 4.01 (3H, s, $COOCH_3$); 6.14 (1H, d, J = 10.0 Hz, CH); 6.89 (2H, d, J = 7.9 Hz, CH); 7.29 (5H, m, CH); 7.40 (1H, d, J = 10.0 Hz, CH); 7.47 (1H, d, J = 7.8 Hz, CH); 7.50 (2H, d, J = 8.3 Hz, CH); 7.62 (1H, dd, J_1 = 7.7, J_2 = 7.0 Hz, CH); 8.33 (2H, d, J = 8.4 Hz, CH); 12.16 (1H, s, OH). HRMS (*m*/*z*): calculated for $[M + H]^+$ 492.2175; found 492.2175.

9,9′-(9-(3-Bromopropyl)-9-methyl-9*H*-fluorene-2,7-diyl)bis-9*H*-carbazole (8a). A solution of bromine (0.06 ml, 1.2 mmol) in anhydrous CH_2Cl_2 (10 ml) was added dropwise to a stirred solution of triphenylphosphine (0.41 g, 1.55 mmol) in the same solvent at room temperature under Ar. After 1 h of stirring the resulting solution was added dropwise to a cooled (0 °C) solution of **7a** (0.57 g, 1 mmol) in anhydrous CH_2Cl_2 (5 ml). After 2 h of additional stirring at room temperature, the mixture was poured into water and extracted with dichloromethane (3 × 50 ml). The extract was washed with water and dried over $MgSO_4$. All volatiles were removed in vacuum and the residue was purified by column chromatography on silica gel with CH_2Cl_2/Hex (1 : 1). After crystallization from MeOH, 0.27 g (83%) of **8a** was obtained as colorless powder, m.p. 172–173 °C. ^{1}H NMR ($CDCl_3$): 1.39 (2H, m, CH_2); 1.63 (3H, s, CH_3); 2.27 (2H, m, CH_2); 3.26 (2H, t, J = 6.2 Hz, CH_2); 7.34 (4H, m, CH); 7.56 (12H, m, CH); 7.99 (2H, d, J = 7.9 Hz, CH); 8.11 (2H, d, J = 7.9 Hz, CH); 8.22 (1H, d, J = 1.5 Hz, CH); 8.27 (1H, d, J = 1.5 Hz, CH). EA: calculated C 77.97, H 4.95, N 4.44; $C_{41}H_{31}BrN_2$; Found C 80.11, H 5.08, N 4.38.

The same procedure afforded (3-bromopropyl)benzene **(8b)** identical to the commercially available sample in 90% yield.

9,9′-(9-(3-Iodopropyl)-9-methyl-9*H*-fluorene-2,7-diyl)bis-9*H*-carbazole (9a). To a solution of **8a** (1 mmol) in acetone (15 ml) dry KI (2 mmol) was added and the mixture was refluxed for 2 h. The inorganic part was filtered off and the filtrate was evaporated. The crude product was crystallized from MeOH, filtered off, washed with water on the filter and dried. **9a** was

obtained in 90% as colorless powder (softens and slowly decomposes above 200 °C). ^{1}H NMR ($CDCl_3$): 1.34 (2H, m, CH_2); 1.62 (3H, s, CH_3); 2.23 (2H, m, CH_2); 3.04 (2H, t, J = 6.5 Hz, CH_2); 7.34 (6H, m, CH); 7.48 (5H, m, CH); 7.54 (2H, ddd, J_1 = 8.0, J_2 = 1.9 Hz, CH); 7.61 (3H, m, CH); 7.98 (2H, d, J = 7.7 Hz, CH); 8.11 (2H, ddd, J_1 = 7.7, J_2 = 0.9 Hz, CH); 8.23 (1H, d, J = 1.9 Hz, CH); 8.27 (1H, d, J = 1.9 Hz, CH). EA: calculated C 72.57, H 4.60, N 4.13; $C_{41}H_{31}IN_2$; Found C 72.41, H 4.72, N 3.98.

The same procedure afforded (3-iodopropyl)benzene **(9b)** identical to the commercially available sample in 95% yield.

A general procedure for compounds 1. A solution of *N*-(3-dimethylaminopropyl)-*N*′-ethylcarbodiimide hydrochloride (EDC) (0.19 g, 1 mmol) in anhydrous CH_2Cl_2 (10 ml) was slowly added to a solution of an appropriate alcohol R-OH (1 mmol), derivative **4** (0.39 g, 1 mmol) and 4-dimethylaminopyridine (DMAP) (0.12 g, 1 mmol) in anhydrous CH_2Cl_2 (10 ml) at 0 °C. The mixture was stirred at room temperature for 48 h. The resulting solution was added to water (30 ml) and extracted with CH_2Cl_2 (3 × 30 ml). The combined organic phase was washed with water (2 × 30 ml), dried over $MgSO_4$, filtered and the solvent was evaporated. The product was purified by column chromatography on a silica gel using a mixture of CH_2Cl_2/hexane (2 : 1) as the eluent.

3-(2,7-Di(9*H*-carbazol-9-yl)-9-methyl-9*H*-fluoren-9-yl)propyl 8-methyl-2,2-diphenyl-2*H*-benzo[*h*]chromene-5-carboxylate (1a). Yield 0.23 g (50%), yellowish powder, colorless after crystallization from acetonitrile, m.p. 181–183 °C. ^{1}H NMR($CDCl_3$): 1.42 (2H, m, CH_2); 1.68 (3H, s, CH_3); 2.30 (2H, ddd, J_1 = 8.1, J_2 = 7.9, J_3 = 3.8 Hz, CH_2); 2.39 (3H, s, CH_3); 4.17 (2H, t, J = 6.5 Hz, CH_2); 6.09 (1H, d, J = 10.1 Hz, CH); 7.26 (11H, m, CH); 7.42 (9H, m, CH); 7.50 (4H, d, J = 8.2 Hz, CH); 7.51 (1H, d, J = 10.1 Hz, CH); 7.64 (2H, dd, J_1 = 8.1, J_2 = 1.9 Hz, CH); 7.73 (2H, d, J = 1.8 Hz, CH); 7.84 (1H, br s, CH); 8.07 (2H, d, J = 8.0 Hz, CH); 8.16 (4H, d, J = 7.7 Hz, CH); 8.23 (1H, d, J = 8.5 Hz, CH). HRMS (*m/z*): calculated for $[M + NH_4]^+$ 960.4160; found 960.4160. EA: calculated C 86.60, H 5.34, N 2.97; $C_{68}H_{50}N_2O_3$; found C 86.53, H 5.44, N 2.88.

3-Phenylpropyl 8-methyl-2,2-diphenyl-2*H*-benzo[*h*]chromene-5-carboxylate (1b). Yield 0.40 g (78%), beige powder, colorless after crystallization from acetonitrile, m.p. 105–107 °C. ^{1}H NMR($CDCl_3$): 2.13 (2H, q, J = 8.1 Hz, CH_2); 2.50 (3H, s, CH_3); 2.82 (2H, t, J = 8.1 Hz, CH_2); 4.36 (2H, t, J = 6.5 Hz, CH_2); 6.22 (1H, d, J = 10.1 Hz, CH); 7.16–7.34 (10H, m, CH); 7.40 (1H, dd, J_1 = 8.6, J_2 = 1.7 Hz, CH); 7.52 (5H, m, CH); 7.57 (1H, br s, CH); 7.66 (1H, d, J = 10.1 Hz, CH); 7.96 (1H, s, CH); 8.28 (1H, d, J = 8.5 Hz, CH). HRMS (*m/z*): calculated for $[M + H]^+$ 511.2268; found 511.2269. EA: calculated C 84.68, H 5.92; $C_{36}H_{30}O_3$; found C 84.56, H 5.83.

A general procedure for compounds 2 and 3. To a solution of derivatives **5** or **6** (0.5 mmol) in 10 ml of acetonitrile, potassium hydroxide (2.0 mmol) was added. The resulting mixture was stirred at room temperature for 0.5 h. Then the corresponding R-I (**9a** or **b**) (0.6 mmol) was added and the stirring was continued at the same temperature for 16–24 h. Acetonitrile was removed in vacuum and the resulting mixture was treated with water and extracted with dichloromethane (3 × 50 ml). The extract was washed with water and dried over $MgSO_4$. All volatiles were removed in vacuum and the crude product was purified by column chromatography on aluminium oxide using CH_2Cl_2/hexane (3 : 2).

Methyl 6-(3-(2,7-di(9*H*-carbazol-9-yl)-9-methyl-9*H*-fluoren-9-yl)propoxy)-2,2-diphenyl-2*H*-benzo[*h*]chromene-5-carboxylate (2a). Yield: 0.11 g (50%), slightly orange powder, m.p. 171–173 °C. ^{1}H NMR ($CDCl_3$): 1.39 (2H, m, CH_2); 1.66 (3H, s, CH_3); 2.31 (2H, m, CH_2); 3.70 (3H, s, $COOCH_3$); 3.83 (2H, t, J = 6.0 Hz, CH_2); 6.17 (1H, d, J = 10.1 Hz, CH); 6.67 (1H, d, J = 10.1 Hz, CH); 7.29 (14H, m, arom); 7.44 (10H, m, arom); 7.58 (2H, dd, J_1 = 8.1, J_2 = 1.8 Hz, CH); 7.65 (2H, d, J = 1.4 Hz, CH); 7.79 (1H, m, CH); 8.01 (2H, d, J = 8.0 Hz, CH); 8.09 (2H, d, J = 8.2 Hz, CH); 8.23 (2H, dd, J_1 = 13.2, J_2 = 1.9 Hz, CH); 8.31 (1H, d, J = 8.3 Hz, CH). HRMS (*m/z*): calculated for $[M + NH_4]^+$ 976.4109; found 976.4109. EA: calculated C 85.15, H 5.25, N 2.92; $C_{68}H_{50}N_2O_4$; found C 84.99, H 5.35, N 2.88.

Methyl 2,2-diphenyl-6-(3-phenylpropoxy)-2*H*-benzo[*h*]chromene-5-carboxylate (2b). Yield: 0.21 g (80%), yellowish powder, m.p. 138–140 °C. ^{1}H NMR ($CDCl_3$): 2.15 (2H, dd, J_1 = 6.8, J_2 = 6.4 Hz CH_2); 2.85 (2H, t, J = 7.8 Hz, CH_2); 3.93 (3H, s, $COOCH_3$); 4.04 (2H, t, J = 6.4 Hz, CH_2); 6.19 (1H, d, J = 10.0 Hz, CH); 6.74 (1H, d, J = 10.0 Hz, CH); 7.27 (10H, m, arom); 7.48 (7H, m, arom); 7.99 (1H, dd, J_1 = 7.3, J_2 = 1.6 Hz, CH); 8.34 (1H, dd, J_1 = 7.5, J_2 = 1.6 Hz, CH). HRMS (*m/z*): calculated for $[M + H]^+$ 527.2217; found 527.2217. EA: calculated C 82.11, H 5.74; $C_{36}H_{30}O_4$; found C 82.16, H 5.76.

Methyl 6-(3-(2,7-di(9*H*-carbazol-9-yl)-9-methyl-9*H*-fluoren-9-yl)propoxy)-2-phenyl-2-(4-(piperidin-1-yl)phenyl)-2*H*-benzo[*h*]chromene-5-carboxylate (3a). Yield: 0.18 g (35%), slightly violet powder, m.p. 211–213 °C. ^{1}H NMR ($CDCl_3$): 1.39 (2H, m, CH_2); 1.55 (4H, m, $C_5H_{10}N$); 1.66 (3H, s, CH_3); 1.69 (2H, m, $C_5H_{10}N$); 2.30 (2H, m, CH_2); 3.13 (4H, m, $C_5H_{10}N$); 3.71 (3H, s, $COOCH_3$); 3.83 (2H, t, J = 6.6 Hz, CH_2); 6.12 (1H, d, J = 10.0 Hz, CH); 6.64 (1H, d, J = 10.0 Hz, CH); 6.88 (1H, m, arom); 7.31 (13H, m, arom); 7.43 (9H, m, arom); 7.57 (1H, d, J = 1.2 Hz, CH); 7.63 (3H, dd, J_1 = 10.6, J_2 = 1.5 Hz, CH); 7.80 (1H, d, J = 8.1 Hz, CH); 8.01 (2H, d, J = 8.1 Hz, CH); 8.10 (1H, d, J = 7.5 Hz, CH); 8.24 (2H, dd, J_1 = 13.4, J_2 = 1.9 Hz, CH); 8.29 (2H, d, J = 8.5 Hz, CH). HRMS (*m/z*): calculated for $[M + NH_4]^+$ 1059.4844; found 1059.4845. EA: calculated C 84.12, H 5.71, N 4.03; $C_{73}H_{59}N_3O_4$; found C 84.07, H 5.88, N 4.11.

Methyl 2-phenyl-6-(3-phenylpropoxy)-2-(4-(piperidin-1-yl)phenyl)-2*H*-benzo[*h*]chromene-5-carboxylate (3b). Yield: 0.14 g (47%), slightly violet powder, m.p. 146–148 °C. ^{1}H NMR ($CDCl_3$): 1.58 (2H, m, $C_5H_{10}N$); 1.76 (4H, m, $C_5H_{10}N$); 2.15 (2H, dd, J_1 = 7.7, J_2 = 6.4 Hz CH_2); 2.84 (2H, dd, J_1 = 8.1, J_2 = 7.5 Hz, CH_2); 3.17 (4H, m, $C_5H_{10}N$); 3.92 (3H, s, $COOCH_3$); 4.04 (2H, t, J = 6.4 Hz, CH_2); 6.15 (1H, d, J = 10.0 Hz, CH); 6.71 (1H, d, J = 10.0 Hz, CH); 7.01 (2H, m, arom); 7.27 (9H, m, arom); 7.48 (5H, m, arom); 7.99 (1H, dd, J_1 = 7.0, J_2 = 1.8 Hz, CH); 8.32 (1H, dd, J_1 = 7.0, J_2 = 1.8 Hz, CH). HRMS (*m/z*): calculated for $[M + H]^+$ 610.2652; found 610.2651. EA: calculated C 80.76, H 6.45, N 2.30; $C_{36}H_{30}NO_4$; found C 80.68, H 6.63, N 2.33.

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