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Intimately bound coumarin and bis(alkylaminostyryl)benzene fragments: synthesis and energy transfer

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ABSTRACT

A novel trichromophoric assembly was synthesized, where two molecules of 7-alkoxy-4-methylcoumarin, acting as energy donors, were linked at a fixed distance and controlled geometry to an energy-acceptor bis(alkylaminostyryl) unit. Resonance energy transfer between the two different species was demonstrated by a careful spectroscopic analysis.

1. Introduction

Resonance energy transfer (RET) phenomena provide the rationale for the optimized design of multichromophoric systems for specific applications, ranging from biosensing[1] to solar energy conversion.[2] RET processes play an essential role in photosynthesis,[3] allowing the funneling of the energy absorbed from light-harvesting complexes toward reaction centers. A deeper understanding of the RET mechanism can lead to significant improvements in enabling technologies, such as photovoltaics[4] or light-emitting devices.[5]

For example, RET processes occurring between different dyes represent an intriguing possibility to improve the performance of luminescent solar concentrators (LSCs).[6] LSC technology relies on the basic concept of separating the two main steps in the photovoltaic process, i.e., the collection of light (optical function) and the generation of charges (electric function). In its simplest design, an LSC consists of a plastic or glassy substrate doped with an organic dye (luminophore). Ideally, the sunlight incident on the front surface of the concentrator is absorbed by the luminophores and subsequently re-emitted at lower energy. Due to total internal reflection, a fraction of the re-emitted photons is trapped within the substrate and is waveguided to the edges of the substrate, where a narrow strip of photovoltaic cells converts the concentrated luminescence into electricity.[7]

The efficiency of LSCs is limited by several loss mechanisms that decrease the internal optical quantum efficiency (OQE) of the device, defined as the fraction of incident photons emitted at the edges of an LSC. An obvious loss mechanism is due to self-absorption within the substrate,[8] a parasitic process where a photon emitted by a luminophore is absorbed by another nearby luminophore. Actually, the re-absorption process does not immediately lead to loss of photon's energy from the system. However, the probability that the photon will be lost through non-radiative decay or through escape cones rises with the rate of self-absorption. In order to increase the OQE, several complementary approaches have been adopted, including the use of luminophores with large Stokes shifts (as to reduce the self-absorption rate), the use of organic chromophores with luminescence quantum yield approaching unity (thus hindering the non-radiative decay loss channel) and the combination of photostable rare earth materials with absorbing species.[6]

RET processes occurring between different dyes offer another intriguing possibility to improve the LSC performance via non-radiative pathways.[9] In this context multichromophoric species containing one or more energy-donor units intimately bound to an

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energy-acceptor unit are interesting models systems for the experimental investigation of RET-related phenomena. On the basis of previous theoretical studies[10] and photophysical properties of similar compounds,[11] we identified acetamido derivatives **1** and **2** as suitable acceptor and donor counterparts, respectively. Together with their synthesis and photophysical characterization, here we report the preparation of the intimately bound assembly **3** (Chart 1) where two donor moieties **2** are covalently linked to one acceptor molecule **1**.

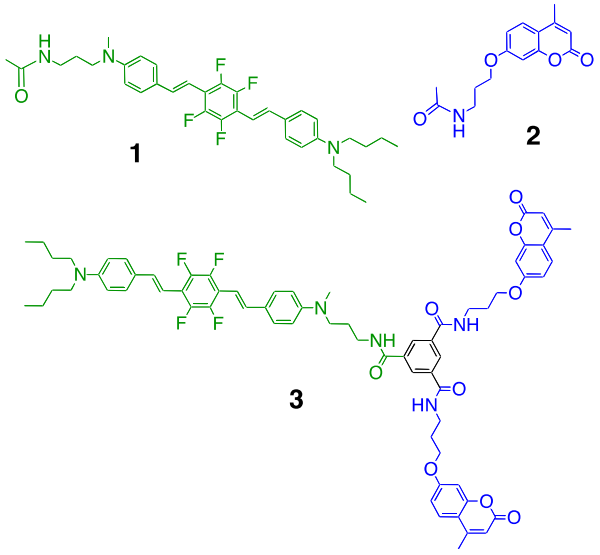


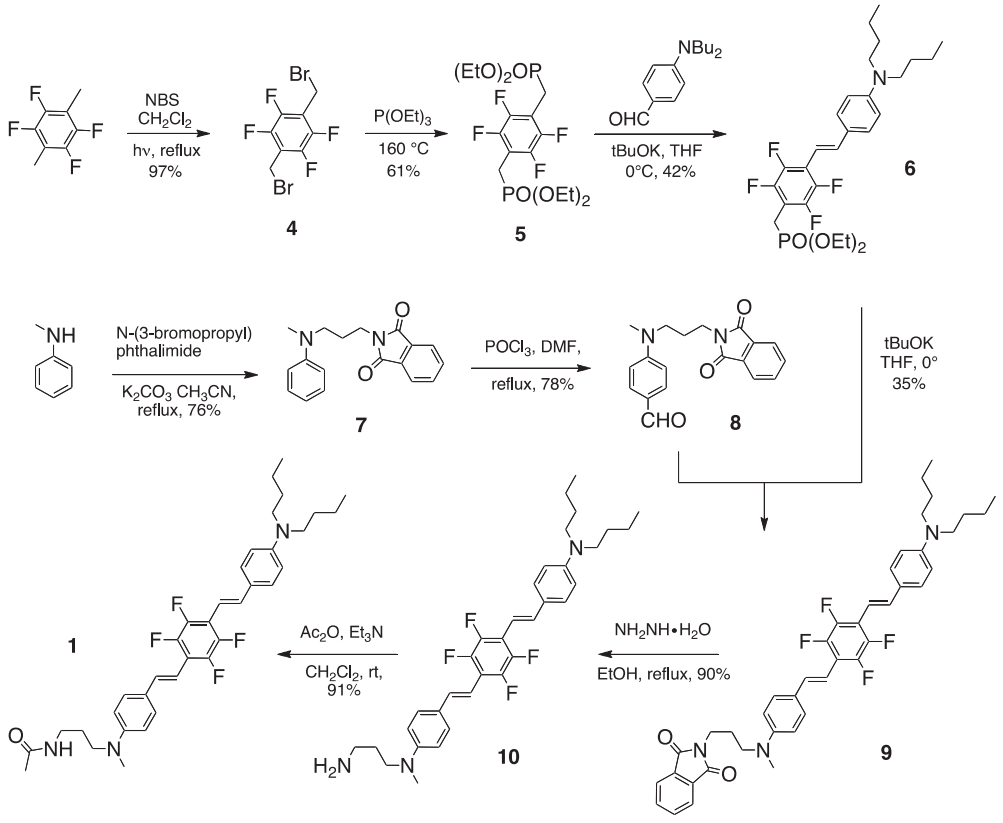
Chart 1. Structures of synthesized acetamido derivatives **1** and **2** and of trichromophoric assembly **3**.

A careful spectroscopic analysis was conducted showing intramolecular resonance energy transfer between the two different species. Moreover, the strong emission observed in the solid state for these dyes makes these systems promising candidates for applications, including, e.g., solar concentrators and organic LEDs, where fluorescence is required from solid state samples with a high fluorophore concentration.

2. Results and discussion

The bis(alkylaminostyryl) **10** and acetamido derivative **1** were prepared according to the synthetic pathway reported in Scheme 1. The bis(phosphonyl) derivative **5** was obtained following similar procedures as reported in the literature,[12] consisting of the dibromination of 2,3,5,6-tetrafluoro-*p*-xylene with *N*-bromosuccinimide and dibenzoylperoxide followed by the reaction of the tetrafluorobis(bromomethyl)benzene **4** with triethyl phosphite. Horner–Emmons reaction between 4-(dibutylamino)benzaldehyde and **5** was carried out in THF at 0 °C affording the dibutylaminostyryl intermediate **6** in 42% yield, together with small amounts (27% yield) of symmetrical bis(dibutylamino)distyryl derivative as byproduct. A subsequent Horner–Emmons condensation between **6** and phthalimido benzaldehyde **8** in the same conditions allowed the formation of phthalimido derivative **9**, which was treated with hydrazine hydrate in refluxing EtOH in order to obtain amine **10** in 90% yield after chromatography. Finally, acetamido compound **1** was prepared in 91% yield by typical reaction of **10** with acetic anhydride in CH_2Cl_2 at room temperature.

A similar synthetic route was followed for the synthesis of coumarin **2** starting from commercially available 7-hydroxy-4-methyl-2*H*-chromen-2-one (See Supplementary data). The sought trichromophoric species **3** was prepared according to the synthetic pathway reported in Scheme 2. Trimesic acid was chosen as scaffold for arranging the chromophores at a fixed distance and controlled



Scheme 1. Synthetic route for the preparation of bis(alkylaminostyryl) **10** and acetamido derivative **1**.

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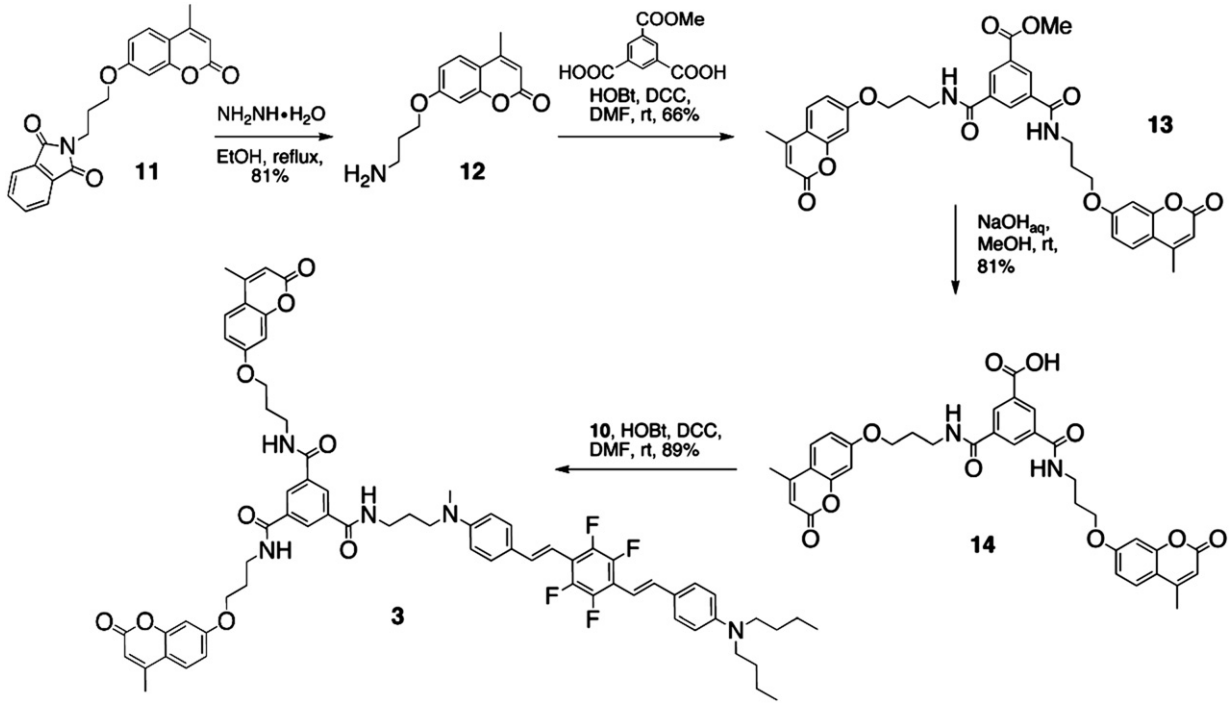

Scheme 2. Synthesis of trichromophoric compound **3**.

geometry and, at the same time, minimizing the interference due to possible radiative transfer processes. The condensation of 2 equiv of aminopropoxy coumarin **12**, obtained in 81% yield from the phthalimido derivative **11**, with 1 equiv of the monomethyl ester of trimesic acid was carried out in anhydrous DMF at room temperature through the activation of the carboxylic acid function with dicyclohexylcarbodiimide (DCC) in the presence of 1-hydroxybenzotriazole (HOBt), following an approach extensively employed in polypeptide synthesis.

The remaining ester group was then hydrolyzed in the presence of aqueous NaOH in MeOH at room temperature. Finally, a second condensation between the carboxylic acid group of **14** and amino-distyryl derivative **10** in conditions similar to the previous ones gave the final compound **3** in good yields (89%) after purification over silica.

Molar extinction coefficients (ε) of the monomers **1** and **2**, and of the trichromophoric specie **3**, are listed in Table 1, and relevant absorption and emission spectra are shown in Fig. 1. The coumarin-based energy donor **2** absorbs in the UV region, and emits in the UV-blue range. Its emission overlaps the absorption band of **1**, the

Table 1
Spectroscopic data referring to EtOH solutions

	ε (M^{-1} cm^{-1})[a]	Φ (%)[b]
1	77,900 at 428 nm	30.0
2	15,100 at 321 nm	11.6
3	77,700 at 428 nm	1.9[c]
	39,600 at 321 nm	

[a] Experimental error: 5%.

[b] Standard for fluorescence quantum yield measurements: fluorescein in NaOH 0.1 M (Φ=90%). Experimental error: 10%. Φ of **1** was evaluated for a solution prepared and stored in the dark; after light-exposure, the emission spectrum of **1** changes, as probably due to a photoinduced *trans–cis* isomerization process. A similar behavior is observed for **3**, but only for the fluorescence band due to the acceptor emission.

[c] The value refers to fluorescence quantum yield of the energy donor, in the presence of the energy acceptor. This value was calculated from emission and absorption spectra of **3**, considering only the contribution of the energy donor, estimated from the comparison with experimental data of **2**.

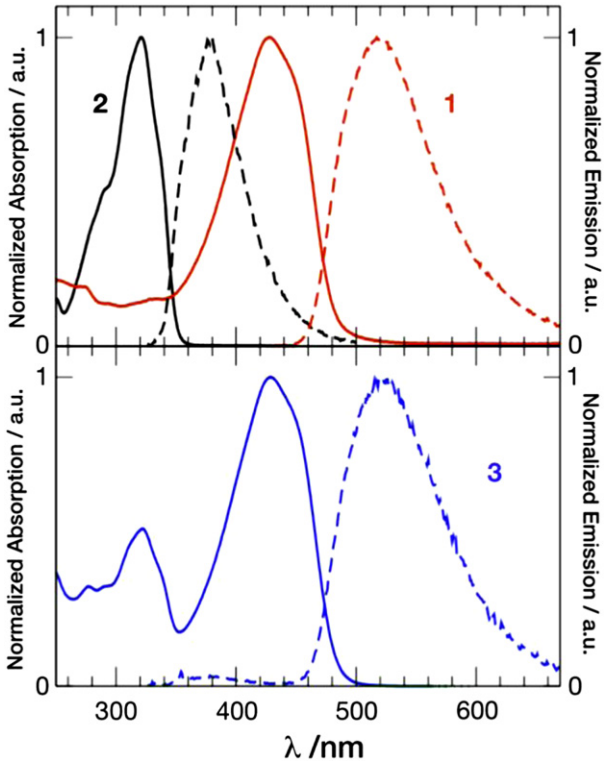

Fig. 1. Top panel: absorption (full line) and emission (dashed line) spectra of **1** and **2** in EtOH. Emission was collected exciting the sample at the maximum of absorption bands (321 nm for **1** and 428 nm for **2**). Bottom panel: absorption (full line) and emission spectra (dashed line) of **3** in EtOH. Emission was collected exciting the sample at 321 nm.

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energy acceptor, which is in turn characterized by a broad emission peaked in the green. The molar extinction coefficient of **3** coincides within experimental error with the sum of the extinction coefficients of one **1** species and two **2** species, suggesting negligible interactions between dyes in the trichromophoric assembly.

The emission spectrum of **3** for excitation at the maximum of absorption of **2**, i.e., 321 nm (bottom panel of Fig. 1) shows a very weak band corresponding to the emission of **2**, and a much more intense peak corresponding to the emission of **1**.

The energy transfer efficiency Φ_T can be estimated as follows:

$$\Phi_T = 1 - \frac{\Phi_D}{\Phi_D^0} \quad (1)$$

where Φ_D and Φ_D^0 are the fluorescence quantum yields of the energy donor in the presence and in the absence of the energy acceptor (i.e., measured for compound **2** and **3**), respectively. As reported in Table 1, the fluorescence quantum yield of the donor is strongly suppressed in the trichromophoric compound **3**, a clear signature of energy transfer. According to the results reported in Table 1, we obtain Φ_T=84%. Following the Förster model,[13] the distance between the energy donor and the energy acceptor is defined as:

$$r = r_0\left(\frac{1}{\Phi_T} - 1\right)^{1/6} \quad (2)$$

where r_0, the Förster radius, measuring the distance corresponding to a 50% transfer efficiency, can be extracted from spectral data as follows:

$$r_0 = 0.2108\left[k^2\Phi_D^0 n^{-4}\int I_D(\lambda)\varepsilon_A(\lambda)\lambda^4 d\lambda\right]^{1/6} \quad (3)$$

In this equation k is an orientational factor (for random relative orientations of the energy donor and the energy acceptor k^2=2/3), n is the refractive index of the medium, $I_D(\lambda)$ is the emission spectrum of the energy-donor, normalized to get unit area, and $\varepsilon_A(\lambda)$ is the molar extinction coefficient of the energy acceptor. The estimated value for r_0 in our case is 36 Å. Equation (2) then leads to r=27 Å, well consistent with the molecular structure. Quite interestingly the energy acceptor is characterized by the presence of a one-photon forbidden (i.e., dark) state in the region of the emission of the donor,[14] that could contribute to enhance the energy-transfer efficiency well beyond the Förster model.[10b] However, an active role of dark states in RET processes is only expected for short interchromophoric distances, where the dipolar approximation does not apply. The estimated interchromophore distance (>20 Å) in **3** is instead fully consistent with the dipolar approximation.

Emission and excitation spectra measured from powders are reported in Fig. 2. Both the monomeric species, **1** and **2**, and the trichromophoric species **3** are highly fluorescent in the solid state, as shown by the photographs in the insets of Fig. 2. All spectra in the solid state are red-shifted with respect to solution spectra, suggesting *J*-like aggregation, in line with the observation of sizable fluorescence. Quite interestingly, the emission spectrum collected from powders of **3** is blue-shifted with respect to the emission spectrum of powders of monomer **1** while both species have basically the same fluorescence spectrum in solution. This implies that the red-shift when going from solution to the solid state is more important for **1** than for **3**, suggesting somewhat reduced intermolecular interactions in this last system. No emission signal from powders of **3** was detected in the 350–500 nm region, corresponding to the emission of the energy-donor, in line with an efficient RET in the solid state. The observation of strong emission from powders suggests that these dyes may find useful application in all those devices, including solar concentrators and organic LEDs, where fluorescence is sought from samples with a high fluorophore concentration.

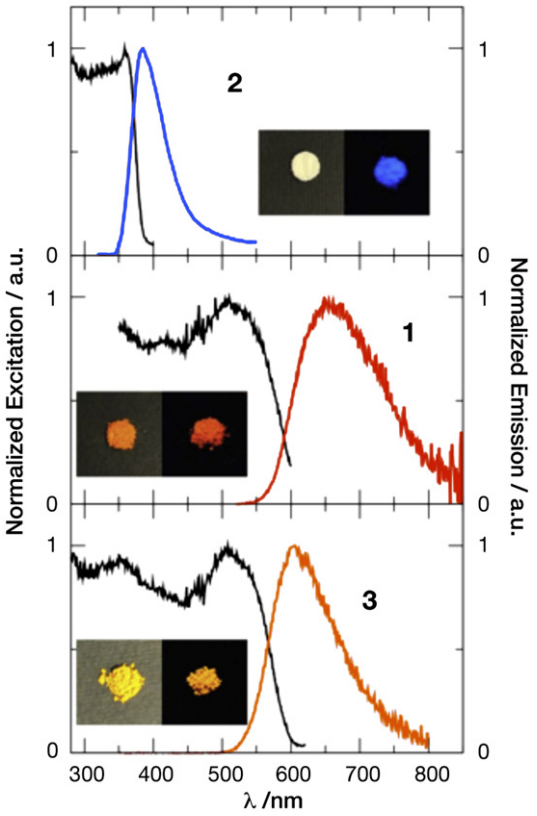

Fig. 2. Excitation and emission spectra of powders of **1**, **2**, and **3**. The inset shows the photo of powders under normal illumination (left) and the photo of powders under exposure to UV light (right, λ_{exc}=365 nm).

3. Conclusion

In summary, we have designed and synthesized a novel trichromophoric molecule containing one bis(alkylaminostyryl) chromophore covalently linked to two 7-alkoxy-4-methylcoumarin through a trimesic acid scaffold. Occurrence of resonance energy transfer between the two different species was demonstrated by photophysical data. The synthetic route adopted and the photophysical behavior observed give insight into the rational design of multichromophore compounds, as well as the fine-tuning of their photophysical properties in order to prepare more efficient RET systems, which can be used in the preparation of luminescent sensitizers.

4. Experimental section

4.1. Materials and methods

All available chemicals and solvents were purchased from commercial sources and were used without any further purification. Thin layer chromatography (TLC) was conducted on plates precoated with silica gel Si 60-F254 (Merck, Darmstadt, Germany). Column chromatography was conducted by using silica gel Si 60, 230–400 mesh, 0.040–0.063 mm (Merck, Darmstadt, Germany). Melting points were determined on a Büchi B450 apparatus and are all uncorrected. FTIR spectra were recorded on an Agilent Cary 630 infrared spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 400 (400 and 100.6 MHz, respectively). Chemical shifts were reported in parts per million downfield from $SiMe_4$, using the residual proton ($CHCl_3$=7.26 ppm, $(CH_3)_2SO$=2.50 ppm, $CHDCl_2$=5.31 ppm) and carbon ($CDCl_3$=77.0 ppm, $(CD_3)_2SO$=40.45 ppm, CD_2Cl_2=53.8 ppm) solvent resonances as internal reference. Protons and carbon assignments were achieved by ^{13}C-APT, ^{1}H–^{1}H COSY, and ^{1}H–^{13}C

heteronuclear correlation experiments. High resolution mass spectra were obtained with an electrospray ion-trap mass spectrometer ICR-FTMS APEX II (Bruker Daltonics) by the Centro Interdipartimentale Grandi Apparecchiature (C.I.G.A.) of the University of Milano. UV–vis absorption spectra were collected on a Perkin–Elmer Lambda650 spectrofluorometer. The Beer–Lambert law was verified in measurements of molar extinction coefficients. Molar extinction coefficients were measured on solutions prepared and stored in the dark, to avoid the light-induced dependence observed for the absorption spectra of **1** and **3**, probably due to a *trans–cis* isomerization process. Emission spectra were measured on a Horiba Jobin-Yvon Fluromax-3 spectrofluorometer. To avoid inner-filter effects, emission spectra were collected on dilute solutions, with absorbance lower than 0.1. Fluorescence quantum yields were measured adopting Fluorescein in NaOH 0.1 M as the standard (Φ=0.9). All spectra were collected in EtOH (J.T. Baker, Absolute).

*4.1.1. 1,2,4,5-Tetrafluoro-3,6-bis(bromomethyl)benzene (**4**).* To a stirred solution of 2,3,5,6-tetrafluoro-*p*-xylene (6.55 g, 37.8 mmol) in CH_2Cl_2 (300 ml) at room temperature was added *N*-bromosuccinimide (20.9 g, 110.3 mmol) and dibenzoylperoxide (1.01 g, 4.17 mmol). The reaction mixture was heated at reflux by irradiation with a 200 W lamp for 18 h. After this time, the solid in suspension progressively disappeared leaving a colorless transparent solution. The cooled reaction was washed with water (3×150 ml), dried over $MgSO_4$ and evaporated under reduced pressure to give the *title compound* **4** (11.9 g, 97%) as a white solid, mp 129–130 °C (lit. [15] mp=125–126 °C). The NMR characterization of the product is consistent with that reported in the literature;[12] δ_H (400 MHz, $CDCl_3$) 4.51 (4H, s, CH_2Br).

*4.1.2. 1,2,4,5-Tetrafluoro-3,6-bis(diethylphosphonylmethyl)benzene (**5**).* A mixture of triethyl phosphite (2.47 g, 14.9 mmol) and **4** (2.00 g, 5.95 mmol) was heated at 160 °C for 4 h. The mixture was then cooled at room temperature. The solid was filtered over a fritted glass septum and washed with diethyl ether to afford the *title compound* **5** (1.63 g, 61%) as a waxy transparent solid, mp 72–73 °C (lit. [12] mp=73–75 °C). The NMR characterization of the product is consistent with that reported in the literature;[12] δ_H (400 MHz, $CDCl_3$) 1.28 (12H, t, *J* 7.1 Hz, $CH_2P(O)OCH_2CH_3$), 3.24 (4H, d, *J* 20.2 Hz, $CH_2P(O)OCH_2CH_3$), 4.10 (8H, m, $CH_2P(O)OCH_2CH_3$).

*4.1.3. (E)-Diethyl 4-(4-(dibutylamino)styryl)-2,3,5,6-tetrafluorobenzylphosphonate (**6**).* A stirred solution of **5** (3.00 g, 6.67 mmol) in anhydrous THF (100 ml) was cooled at 0 °C under a nitrogen atmosphere. Solid potassium *tert*-butoxide (0.686 g, 6.11 mmol) was added and the resulting orange-red mixture was left stirring for 5 min. Then a solution of 4-(dibutylamino)benzaldehyde (1.30 g, 5.56 mmol) in anhydrous THF (10 ml) was added dropwise. The progressive consumption of the aldehyde was monitored by TLC over silica plates (hexane/AcOEt 9:1). After 2 h water (50 ml) and a saturated aqueous solution of NH_4Cl (20 ml) were added. The organic phase was separated and the aqueous phase was washed with AcOEt (2×40 ml). The combined organic phases were dried over $MgSO_4$ and the solvents evaporated under reduced pressure. Purification of the residue by column chromatography (SiO_2; EtP/AcOEt 9:1 to 2:1) afforded pure *title compound* **6** (1.25 g, 42%) as red-orange crystals and disubstituted *4,4′-(1E,1′E)-2,2′-(perfluoro-1,4-phenylene)bis(ethene-2,1-diyl)bis(N,N-dibutylaniline)* (0.460 g, 27%) as by-product. **6**: mp=85–87 °C; ν_{max}(KBr) 2957, 2931, 2871, 1599, 1523, 1485, 1326, 1269, 1187, 1055, 1030, 983, 949, 807 cm^{-1}; δ_H (400 MHz, CD_2Cl_2) 0.95 (6H, t, *J* 7.4 Hz, CH_3), 1.27 (6H, t, *J* 7.1 Hz, CH_2), 1.35 (4H, sex, *J* 7.4 Hz, CH_2), 1.57 (4H, m, CH_2), 3.22 (2H, d, *J* 21 Hz, CH_2PO), 3.30 (4H, m, CH_2), 4.07 (4H, m, CH_2O), 6.64 (2H, d, *J* 5.1 Hz, ArH), 6.80 (1H, d, *J* 17 Hz, *H*-styryl), 7.37 (3H, m, *H*-styryl, ArH); δ_C (100.6 MHz, CD_2Cl_2) 14.1, 16.5, 20.7, 21.9 (d, *J* 155.0 Hz), 29.8, 51.0, 62.8 (d, *J* 7.5 Hz), 108.2, 108.4 (m), 111.8, 117.4 (br t, *J* 13.7 Hz), 123.8, 128.7, 129.9, 137.8 (br t, *J* 8.8 Hz), 143.7 (m), 146.2 (m), 149.3; HRMS (ESI): MNa^+, found 552.22582. $C_{27}H_{36}F_4NNaO_3P$ requires 552.22611. *4,4′-(1E,1′E)-2,2′-(perfluoro-1,4-phenylene)bis(ethene-2,1-diyl)bis(N,N-dibutylaniline)*: δ_H (400 MHz, CD_2Cl_2) 0.96 (12H, t, *J* 7.4 Hz, CH_3), 1.35 (8H, sex, *J* 7.4 Hz, CH_2), 1.53–1.61 (8H, m, CH_2), 3.30 (8H, m, CH_2),6.63 (4H, d, *J* 8.9 Hz, ArH), 6.81 (2H,d, *J* 16.7 Hz, *H*-styryl),7.37 (4H, d, *J* 8.9 Hz, ArH),7.42 (2H, d, *J* 16.7 Hz, *H*-styryl); δ_C (100.6 MHz, CD_2Cl_2) 14.1, 20.7, 29.8, 51.0, 108.2, 111.8, 113.1 (t, *J* 13.7 Hz), 117.8 (t, *J* 13.7 Hz), 121.8 (m), 123.8, 128.9, 138.3 (t, *J* 8.3 Hz), 143.8 (m), 146.2 (m), 149.4.

*4.1.4. 2-(3-(Methyl(phenyl)amino)propyl)isoindoline-1,3-dione (**7**).* To a solution of freshly distilled *N*-methylaniline (3.65 g, 34.1 mmol) in CH_3CN (100 ml) were added *N*-(3-bromopropyl) phthalimide (11.0 g, 41.0 mmol) and K_2CO_3 (19 g, 135.7 mmol). The mixture was stirred at reflux for 18 h. After cooling at room temperature, the solid was filtered over a fritted glass septum and washed with CH_3CN (2×20 ml). The filtrate was concentrated to dryness under reduced pressure. The residue so obtained was purified by column chromatography (SiO_2; hexane/AcOEt 9:1) to give the *title compound* **7** (7.63 g, 76%) as a pale brown solid, mp 75–77 °C; ν_{max}(KBr) 3059, 2953, 2924, 1766, 1712, 1597, 1510, 1394, 1357 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 1.98 (2H, quin, *J* 7.3 Hz, CH_2), 2.93 (3H, s, NCH_3), 3.39 (2H, t, *J* 7.3 Hz, CH_2), 3.74 (2H, t, *J* 7.3 Hz, CH_2), 6.72–6.67 (3H, m, ArH), 7.21 (2H,dd, *J* 8.6, 7.3 Hz, ArH), 7.74–7.71 (2H, m, ArH), 7.86–7.83 (2H, m, ArH); δ_C (100.6 MHz, $CDCl_3$) 26.0, 35.8, 38.6, 50.3, 112.3, 116.3, 122.9, 128.9, 132.0, 133.3, 149.3, 168.2. HRMS (ESI): MNa^+, found 317.12643. $C_{18}H_{18}N_2NaO_2$ requires 317.12605.

*4.1.5. 4-((3-(1,3-Dioxoisoindolin-2-yl)propyl)(methyl)amino)benzaldehyde (**8**).* A mixture of anhydrous DMF (35 ml) and $POCl_3$ (1.68 g, 11.0 mmol) was stirred under a nitrogen atmosphere at 0 °C for 1.5 h, then at room temperature for 1 h. The yellow solution was then heated at 95 °C and a solution of **7** (2.94 g, 10.0 mmol) in anhydrous DMF (10 ml) was added and the resulting mixture was stirred at 95 °C for 4 h. The solvent was removed under reduced pressure, the residue was taken up with water (50 ml) and the pH was adjusted at 7–8 by addition of sodium bicarbonate saturated aqueous solution. The organic phase was extracted with CH_2Cl_2 (3×50 ml). The organic phase was washed with water (2×50 ml), dried over $MgSO_4$ and the solvent evaporated under reduced pressure to afford a brown oil residue that was purified by column chromatography (SiO_2; hexane/AcOEt 9:1) to afford the *title compound* **8** (2.78 g, 78%) as a brown solid, mp 126–128 °C; ν_{max}(KBr) 2946, 2911, 2811, 2740, 1764, 1707, 1600, 1375, 1168 cm^{-1}; δ_H (400 MHz, $CDCl_3$)2.03 (2H, quin, *J* 7.3 Hz, CH_2), 3.01 (3H, s, NCH_3), 3.50 (2H, m, CH_2), 3.75 (2H, t, *J* 7.3 Hz, CH_2), 6.68 (2H,d, *J* 9.0 Hz, ArH), 7.73–7.69 (4H, m, ArH), 7.86–7.84 (2H, m, ArH), 9.72 (1H, s, C*H*O); δ_C (100.6 MHz, $CDCl_3$) 26.1, 35.7, 38.4, 49.9, 111.1, 123.3, 125.4, 132.0, 132.1, 134.0, 153.3, 168.3, 190.2; HRMS (ESI): MNa^+, found 345.12142. $C_{19}H_{18}N_2NaO_3$ requires 345.12096.

*4.1.6. (E,E)-1-(4(Dibutylamino)styryl)-4-(((3-(1,3-dioxoisoindolin-2-yl)propyl)(methyl)amino)styryl)-2,3,5,6-tetrafluorobenzene (**9**).* A stirred solution of **6** (0.930 g, 1.76 mmol) in anhydrous THF (30 ml) was cooled at 0 °C under a nitrogen atmosphere. Solid potassium *tert*-butoxide (0.217 g, 1.93 mmol) was added and the resulting dark-red solution was stirred at 0 °C for 5 min. Then a solution of **8** (0.737 g, 2.29 mmol) in anhydrous THF (10 ml) was added dropwise, keeping the temperature below 5 °C. After 3 h, a saturated aqueous solution of NH_4Cl (60 ml) was added, the organic phase was separated and the aqueous phase was washed with CH_2Cl_2 (2×40 ml). The combined organic phases were dried over $MgSO_4$ and the solvents removed under reduced pressure. Purification of the residue required two consecutive steps of silica column chromatography (first: CH_2Cl_2/MeOH 7:3; second: CH_2Cl_2) in order to

obtain the *title compound* **9** (0.430 g, 42%) as a crystalline red solid, mp 195–196 °C; ν_{max}(KBr) 3036, 2957, 2930, 2871, 1762, 1702, 1600, 1532, 1377 cm^{-1}; δ_H (400 MHz, CD_2Cl_2) 0.96 (6H, t, *J* 7.4 Hz, CH_3), 1.35 (4H, sex, *J* 7.4 Hz, CH_2), 1.58 (4H, m, CH_2), 1.98 (2H, quin, *J* 7.2 Hz, CH_2), 2.98 (3H, s, NCH_3), 3.30 (4H, br t, *J* 7.5 Hz, CH_2), 3.44 (2H, br t, *J* 7.2 Hz, CH_2), 3.72 (2H, t, *J* 7.2 Hz, CH_2), 6.64 (2H, d, *J* 8.9 Hz, ArH), 6.68 (2H, d, *J* 8.9 Hz, ArH), 6.83 (1H, d, *J* 16.7 Hz, *H*-styryl), 6.85 (1H, d, *J* 16.7 Hz, *H*-styryl), 7.42–7.36 (6H, m, ArH, *H*-styryl), 7.75–7.70 (2H, m, ArH), 7.85–7.80 (2H, m, ArH); δ_C (100.6 MHz, CD_2Cl_2)14.1, 20.7, 26.3, 29.8, 36.2, 38.5, 50.3, 51.0, 108.7, 109.5, 111.8, 112.4, 114.7 (m), 115.2 (m), 123.4, 124.0, 125.2, 128.5, 128.6, 132.5, 134.3, 136.7 (m), 137.0 (m), 143.6 (m), 146.0 (m), 149.1, 149.9, 168.6. HRMS (ESI): MNa^+, found 720.31928. $C_{42}H_{43}F_4N_3NaO_2$ requires 720.31891.

*4.1.7. N^1-(4-(4-(4-(Dibutylamino)styryl)-2,3,5,6-tetrafluorostyryl) phenyl)-N^1-methylpropane-1,3-diamine (**10**).* To a suspension of **9** (0.210 g, 0.301 mmol) in absolute EtOH (25 ml) was added hydrazine monohydrate (0.103 g, 2 mmol) at room temperature and then the mixture was treated at reflux. The reaction was followed by TLC over silica plates (CH_2Cl_2/MeOH 8:2). After approximately 8 h, the starting product **9** was undetectable. The mixture was cooled at room temperature and filtered over a fritted glass septum. The solid was washed with EtOH (5 ml) and MeOH (5 ml). The filtrate was evaporated under reduced pressure. The residue was purified by column chromatography (SiO_2; CH_2Cl_2/MeOH/aqNH_3 9:1:0.1) to give the *title compound* **10** (0.154 g, 90%) as a bright orange solid, mp 125–127 °C; ν_{max}(KBr) 3425, 2954, 2929, 2870, 1600, 1521, 1480, 1368, 1188; δ_H (400 MHz, CD_2Cl_2+1% CD_3OD) 0.95 (6H, t, *J* 7.4 Hz, CH_3), 1.36 (4H, sex, *J* 7.4 Hz, CH_2), 1.57 (4H, m, CH_2), 1.77 (2H, quin, *J* 7.1 Hz, CH_2), 2.74 (2H, t, *J* 7.1 Hz, CH_2), 2.96 (3H, s, NCH_3), 3.29 (4H, br t, *J* 7.6 Hz, CH_2), 3.41 (2H, t, *J* 7.4 Hz, CH_2), 6.62 (2H, d, *J* 8.9 Hz, ArH), 6.68 (2H, d, *J* 8.9 Hz, ArH), 6.82 (1H, d, *J* 16.6 Hz, *H*-styryl), 6.84 (1H, d, *J* 16.6 Hz, *H*-styryl), 7.36–7.42 (6H, m, *H*-styryl, ArH); δ_C (100.6 MHz, CD_2Cl_2+1% CD_3OD) 14.1, 20.7, 29.8, 30.0, 38.5, 39.6, 50.4, 51.1, 111.9, 112.4, 114.7 (m), 115.2 (m), 124.2, 125.3, 128.6, 136.8, 137.1, 143.7 (m), 146.1 (m), 149.2, 150.1; HRMS (ESI): MH^+, found 568.33072. $C_{34}H_{42}F_4N_3$ requires 568.33094.

*4.1.8. N-(3-((4-(4-(4-(Dibutylamino)styryl)-2,3,5,6-tetrafluorostyryl) phenyl)(methyl)amino)propyl)acetamide (**1**).* To a solution of **10** (0.150 g, 0.264 mmol) in anhydrous CH_2Cl_2 (10 ml) and Et_3N (72.6 mg, 0.72 mmol) was added acetic anhydride (54 mg, 0.53 mmol) at room temperature. The mixture was stirred for 4 h, then a saturated aqueous solution of $NaHCO_3$ (10 ml) was added. The organic phase was separated and the aqueous one was washed with CH_2Cl_2 (2×5 ml). The combined organic solutions were dried over $MgSO_4$ and evaporated to dryness. The residue was purified by column chromatography (SiO_2; CH_2Cl_2/MeOH 98:2) to afford the *title compound* **1** (0.210 g, 91%) as an orange solid, mp 181–183 °C; ν_{max}(KBr) 3306, 2954, 2929, 2869, 1599, 1523, 1368, 1189 cm^{-1}; δ_H (400 MHz, CD_2Cl_2) 0.96 (6H, t, *J* 7.3 Hz, CH_3), 1.35 (4H, sex, *J* 7.3 Hz, CH_2), 1.53–1.61 (4H, m, CH_2), 1.77 (2H, quin, *J* 7.1 Hz, CH_2), 1.91 (3H, s, NCOCH_3), 2.97 (3H, s, NCH_3), 3.22–3.32 (6H, m, CH_2), 3.40 (2H, t, *J* 7.1 Hz, CH_2), 5.52 (1H, br s, N*H*), 6.62 (2H, d, *J* 8.8 Hz, ArH), 6.68 (2H, d, *J* 8.8 Hz, ArH), 6.83 (1H, d, *J* 16.8 Hz, *H*-styryl) 6.87 (1H, d, *J* 16.8 Hz, *H*-styryl), 7.37–7.44 (6H, m, *H*-styryl, ArH); δ_C (100.6 MHz, CD_2Cl_2) 14.1, 20.7, 23.4, 27.5, 29.8, 37.8, 38.6, 50.4, 51.0, 108.7, 109.5, 111.8, 112.3, 114.7, 115.3, 124.0, 124.9, 128.6, 136.7, 137.0, 143.6, 146.0, 149.1, 150.0. HRMS (ESI): MH^+, found 610.34259. $C_{36}H_{44}F_4N_3O$ requires 610.34150; MNa^+, found 632.32415. $C_{36}H_{43}F_4N_3NaO$ requires 632.32345.

*4.1.9. 2-(3-(4-Methyl-2-oxo-2H-chromen-7-yloxy)propyl)isoindoline-1,3-dione (**11**).* To a solution of 7-hydroxy-4-methyl-2*H*-chromen-2-one (2.0 g, 11.4 mmol) in acetone (130 ml) were added as solids *N*-(3-bromopropyl)phthalimide (4.6 g, 17.1 mmol), NaI (0.342 g, 2.28 mmol) and K_2CO_3 (8.1 g, 57.0 mmol). The resulting suspension was heated at reflux for 12 h. After this time, it was cooled at room temperature and the solid removed by filtration over a fritted septum. The organic solvent was removed by evaporation under reduced pressure and the residue was purified by column chromatography (SiO_2; $CHCl_3$) to afford the *title compound* **11** (3.40 g, 81%) as a white solid, mp 189–191 °C; ν_{max}(KBr) 2981, 2939, 1762, 1736, 1711, 1614, 1405, 1392 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 2.22 (2H, quin, *J* 6.3 Hz, CH_2), 2.38 (3H, d, *J* 1.2 Hz, CH_3Ar), 3.93 (2H, t, *J* 6.3 Hz, CH_2), 4.08 (2H, t, *J* 6.3 Hz, CH_2), 6.12 (1H, m, ArH), 6.70 (1H, d, *J* 2.5 Hz, ArH), 6.75 (1H, dd, *J* 8.8, 2.5 Hz, ArH), 7.45 (1H, d, *J* 8.8 Hz, ArH), 7.70–7.75 (2H, m, ArH), 7.82–7.86 (2H, m, ArH); δ_C (100.6 MHz, $CDCl_3$) 18.6, 28.1, 35.3, 66.2, 101.5, 112.0, 112.4, 113.7, 123.3, 125.5, 132.1, 134.0, 152.5, 155.2, 161.2, 161.7, 168.3; HRMS (ESI): MNa^+, found 386.10029. $C_{21}H_{17}NNaO_5$ requires 386.09989.

*4.1.10. 7-(3-Aminopropoxy)-4-methyl-2H-chromen-2-one (**12**).* To a suspension of **11** (1.5 g, 4.13 mmol) in MeOH (60 ml) was added hydrazine monohydrate (0.310 g, 6.20 mmol) at room temperature. The mixture was treated at reflux until complete consumption of starting product was confirmed by TLC over silica plates ($CHCl_3$). Then the solvent was evaporated under reduced pressure and the solid residue was purified by column chromatography (neutral Al_2O_3; CH_2Cl_2/MeOH/30%-aqNH_3 9:1:0.1) to give the *title compound* **12** (0.789 g, 82%) as a yellow solid, mp 137–138 °C; ν_{max}(KBr) 3319, 2942, 2871, 1713, 1618, 1388, 1291, 1150 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 1.96 (2H, quin, *J* 6.5 Hz, CH_2), 2.39 (3H, d, *J* 1.2 Hz, CH_3Ar), 2.93 (2H, t, *J* 6.5 Hz, CH_2), 4.12 (2H, t, *J* 6.5 Hz, CH_2), 6.12 (1H, m, ArH), 6.82 (1H, d, *J* 2.4 Hz, ArH), 6.84 (1H, dd, *J* 8.8, 2.4 Hz, ArH), 7.48 (1H, d, *J* 8.8 Hz, ArH); δ_C (100.6 MHz, $CDCl_3$) 18.6, 32.7, 39.0, 66.4, 101.5, 111.9, 112.6, 113.6, 125.5, 152.4, 155.3, 161.3, 162.1; HRMS (ESI): MH^+, found 234.11252. $C_{13}H_{16}NO_3$ requires 234.11247.

*4.1.11. N-(3-(4-Methyl-2-oxo-2H-chromen-7-yloxy)propyl)acetamide (**2**).* To a solution of **12** (0.480 g, 2.06 mmol) in anhydrous CH_2Cl_2 (20 ml) and Et_3N (0.624 g, 6.18 mmol) was added acetic anhydride (0.540 g, 5.29 mmol) at room temperature. The mixture was stirred for 6 h, then a saturated aqueous solution of $NaHCO_3$ (20 ml) was added. The organic phase was separated and the aqueous one was washed with CH_2Cl_2 (2×10 ml). The combined organic solutions were dried over $MgSO_4$ and evaporated to dryness. The residue was purified by column chromatography (SiO_2; CH_2Cl_2/MeOH 95:5) to afford the *title compound* **2** (0.488 g, 86%) as a white solid, mp 129–131 °C; ν_{max}(KBr) 3438, 3278, 3087, 1710, 1620, 1568, 1390, 1282 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 1.99 (3H, s, NCOCH_3), 2.04 (2H, quin, *J* 6.4 Hz, CH_2), 2.38 (3H, d, *J* 1.1 Hz, CH_3Ar), 3.46 (2H, q, *J* 6.4 Hz, CH_2), 4.08 (2H, t, *J* 6.4 Hz, CH_2), 5.95 (1H, br s, N*H*), 6.11 (1H, d, *J* 1.1 Hz, ArH), 6.77 (1H, d, *J* 2.5 Hz, ArH), 6.83 (1H, dd, *J* 8.8, 2.5 Hz, ArH), 7.47 (1H, d, *J* 8.8 Hz, ArH); δ_C (100.6 MHz, $CDCl_3$) 18.7, 23.3, 28.9, 37.0, 66.4, 101.5, 112.0, 112.4, 113.7, 125.6, 152.6, 155.2, 161.3, 161.7, 170.4; HRMS (ESI): MNa^+, found 298.10507. $C_{15}H_{17}NNaO_4$ requires 298.10498.

*4.1.12. Methyl 3,5-bis(3-(4-methyl-2-oxo-2H-chromen-7-yloxy)propylcarbamoyl)benzoate (**13**).* To a solution of **12** (1.20 g, 5.15 mmol) and 5-(methoxycarbonyl)trimesic acid (0.384 g, 1.72 mmol) in anhydrous DMF (20 ml) was added solid 1*H*-benzo[*d*][1,2,3]triazol-1-ol (0.697 g, 5.15 mmol). The mixture was left stirring at room temperature under inert atmosphere for 1 h and then a solution of dicyclohexylcarbodiimide (1.00 g, 4.85 mmol) in anhydrous DMF (10 ml) was added dropwise. The reaction mixture was left under stirring at room temperature for 48 h. The solvent was removed under reduced pressure and the residue was redissolved in CH_2Cl_2 (150 ml). This solution was washed with H_2O (3×80 ml) and the organic phase was collected. The residue obtained by evaporation of the organic solvent under reduced pressure was purified by

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column chromatography (SiO_2; AcOEt/MeOH 100:1) to afford a yellowish solid, which was washed with boiling MeOH (80 ml) to give the *title compound* **13** (0.774 g, 66%) as a white fluffy solid, mp 190–192 °C; ν_{max}(KBr) 3349, 3077, 2948, 1721, 1614, 1540, 1265, 1147 cm^{-1}; δ_H (400 MHz, DMSO-d_6) 2.01 (4H, quin, *J* 6.4 Hz, CH_2), 2.37 (6H, br s, CH_3Ar), 3.45 (4H, dd, *J* 6.4, 5.6 Hz, CH_2), 3.89 (3H, s, COOCH_3), 4.14 (4H, t, *J* 6.4 Hz, CH_2), 6.18 (2H, br s, ArH), 6.92–6.95 (4H, m, ArH), 7.64 (2H, d, *J* 9.6 Hz, ArH), 8.52 (2H, br d, *J* 1.6 Hz, ArH), 8.56 (1H, br t, *J* 1.6 Hz, ArH), 8.90 (2H, br t, *J* 5.6 Hz, N*H*); δ_C (100.6 MHz, DMSO-d_6) 18.1, 28.5, 36.5, 52.5, 66.2, 101.2, 111.1, 112.4, 113.1, 126.4, 129.8, 130.1, 130.8, 135.3, 153.4, 154.7, 160.1, 161.7, 164.9, 165.4; HRMS (ESI): MNa^+, found 677.21003. $C_{36}H_{34}N_2NaO_{10}$ requires 677.21057.

*4.1.13. 3,5-Bis(3-(4-methyl-2-oxo-2H-chromen-7-yloxy)propylcarbamoyl)benzoic acid (**14**).* To a suspension of **13** (0.190 g, 0.29 mmol) in MeOH (20 ml) was added a 0.5 M aqueous solution of NaOH (2 ml, 1.00 mmol) at room temperature. The mixture was stirred at reflux until the disappearance of the solid. Then the solution was cooled at room temperature and the organic solvent removed under reduced pressure. The residue was redissolved in H_2O (10 ml) and the aqueous solution was acidified to pH 3 with 10% HCl (approximately 10 ml). The white solid was filtered, dried in vacuum and purified by column chromatography (SiO_2; CH_2Cl_2/MeOH 9:1) to give the *title compound* **14** (0.150 g, 81%) as a white solid, mp 200–202 °C; ν_{max}(KBr) 3342, 3079, 2931, 2881, 1710, 1613, 1553, 1389, 1284, 1147 cm^{-1}; δ_H (400 MHz, DMSO-d_6) 2.00 (4H, quin, *J* 6.4 Hz, CH_2), 2.35 (6H, br s, CH_3Ar), 3.43 (4H, dd, *J* 6.4, 5.6 Hz, CH_2), 4.12 (4H, t, *J* 6.4 Hz, CH_2), 6.17 (2H, br s, ArH), 6.90–6.93 (4H, m, ArH), 7.61 (2H, d, *J* 9.6 Hz, ArH), 8.37 (1H, br s, ArH), 8.54 (2H, br s, ArH), 8.87 (2H, br t, *J* 5.6 Hz, N*H*); δ_C (100.6 MHz, DMSO-d_6) 18.6, 29.2, 36.8, 66.8, 101.6, 111.5, 112.8, 113.5, 126.9, 128.0, 130.9, 134.7, 153.8, 155.2, 160.6, 162.2, 166.6; HRMS (ESI): $(M-H)^-$, found 639.19815. $C_{35}H_{31}N_2O_{10}$ requires 639.19842.

*4.1.14. N^1-(3-((4-(4-(4-(Dibutylamino)styryl)-2,3,5,6-tetrafluorostyryl)phenyl)(methyl)amino)propyl)-N^3,N^5-bis(3-(4-methyl-2-oxo-2H-chromen-7-yloxy)propyl)benzene-1,3,5-tricarboxamide (**3**).* To a solution of **14** (0.150 g, 0.22 mmol) and **10** (0.253 g, 0.446 mmol) in anhydrous DMF (20 ml) was added solid 1*H*-benzo[*d*][1,2,3]triazol-1-ol (60 mg, 0.446 mmol). The mixture was left stirring at room temperature under inert atmosphere for 1 h and then a solution of dicyclohexylcarbodiimide (92 mg, 4.85 mmol) in anhydrous DMF (5 ml) was added. The reaction mixture was left under stirring at room temperature for 5 d. The solvent was removed under reduced pressure and the residue was redissolved in CH_2Cl_2 (150 ml). This solution was washed with H_2O (3×60 ml) and the organic phase was collected. The residue obtained by evaporation of the organic solvent under reduced pressure was purified by column chromatography (SiO_2; CH_2Cl_2/MeOH 100:1 to CH_2Cl_2/MeOH/30%-aqNH_3 9:1:0.1) to afford the *title compound* **3** (0.240 g, 89%) as an orange solid, mp 124–126 °C; ν_{max}(KBr) 3370, 2929, 2871, 1712, 1661, 1599, 1521, 1283, 1186, 1145; δ_H (400 MHz, CD_2Cl_2) 0.96 (6H, t, *J* 7.2 Hz), 1.35 (4H, sex, *J* 7.2 Hz), 1.58 (4H, m, CH_2), 1.89 (2H, quin, *J* 7.2 Hz, CH_2), 2.09 (4H, quin, *J* 6.0 Hz, CH_2), 2.30 (6H, d, *J* 1.2 Hz, CH_3Ar), 2.94 (3H, s, NCH_3), 3.30 (4H, m, CH_2), 3.41–3.49 (4H, m, CH_2), 3.62 (4H, q, *J* 6.0 Hz, CH_2), 4.08 (4H, t, *J* 7.2 Hz), 6.02 (2H, d, *J* 1.2 Hz, ArH), 6.61–6.68 (6H, m, ArH, *H*-styryl), 6.78–6.84 (6H, m, ArH, *H*-styryl), 6.95 (1H, br t, *J* 5.6 Hz, N*H*), 7.18 (2H, br t, *J* 5.6 Hz, N*H*), 7.31–7.42 (8H, m, ArH), 8.34 (2H, d, *J* 1.6 Hz, ArH), 8.40 (1H, br t, *J* 1.6 Hz, ArH); δ_C (100.6 MHz, CD_2Cl_2) 14.1, 18.8, 20.7, 27.2, 29.2, 29.8, 37.7, 37.8, 38.5, 50.4, 51.0, 67.0, 101.4, 108.6, 109.5, 111.8, 112.0, 112.4, 112.7, 113.9, 114.6, 115.2, 124.0, 125.2, 126.0, 128.6 (2C), 135.5, 136.6, 137.0, 143.5, 145.9, 149.1, 149.9, 153.2, 155.4, 161.4, 162.0, 166.1; HRMS (ESI): MNa^+, found1212.50942. $C_{69}H_{71}F_4N_5NaO_9$ requires 1212.50801.

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Supplementary data

Scheme of the synthesis of amino coumarin **10** and acetamido derivative **2**, ^1H NMR and ^{13}C NMR spectra of all new compounds are given. Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.tet.2013.01.075.

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