Supporting Information

Enhancing the photochromic properties of naphthopyrans via the control of polymeric architectures.

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Experimental Section

General Data, Materials

All solvents, monomers, and other reagents were purchased from Aldrich at the highest purity available. Methyl methacrylate (MMA, 99%) and methyl acrylate (MA, 99%) were filtered before utilization through a basic alumina (Brockmann I) column, to remove the radical inhibitor. Azobis(isobutyronitrile) (AIBN, 99%) was recrystallised twice from ethanol. 2-(2-cyanopropyl)dithiobenzoate (CPDB) was synthesized following a published procedure.[1] Air-and moisture sensitive compounds were manipulated using standard Schlenk techniques under a nitrogen atmosphere.

Equipment

Size Exclusion Chromatography. Molecular weight distributions were recorded using size exclusion chromatography (SEC) at ambient temperature using a system equipped with a Polymer Laboratories 5.0 μm-bead-size guard column (50 × 7.5 mm) and two Polymer Laboratories Plgel 5 μm MIXED-C columns (molecular weight range of 2 000 000-500) with a differential refractive index detector (Shodex, RI-101). Tetrahydrofuran was used as an eluent at flow rate of 1 $mL.min^{-1}$, and toluene was used as flow rate marker. Poly(methyl methacrylate) in the range of 1 944 000-1020 were used for calibration.

^{1}H NMR Spectroscopy. ^{1}H NMR (400 MHz) spectra were recorded on a Bruker 400 UltraShield spectrometer at 25°C and d-chloroform was used as solvent. Chemical shifts, expressed in ppm, are reported as δ values relative to TMS.

UV-Vis. The polymeric films were formed by dissolving the polymer in THF in order to obtain a viscous liquid, which was spread on microscope glass slides (Menzel-Gläser). After drying 2 days at room temperature, the films were irradiated and anlaysed in an UV-Vis spectrophotometer Analytik Jena Specord S100 (Carl Zeiss Technology).

For the organic syntheses, reaction progress was followed by thin-layer chromatography on Merck silica gel plates 60 F_{254}. The products were visualised by UV (254/366 nm). Column chromatography was carried out on silica gel (Fisher Chemicals, particle size: 35-70 microns, 60 Å)

4-Hydroxy-4'-methoxybenzophenone (1)

A mixture of anisole (5.4 g, 49.93 mmol) and 4-hydroxybenzoic acid (7.59 g, 54.95 mmol) in methanesulfonic acid (65 mL) was stirred at 70-75°C for 42 hours. The solution was cooled to room temperature and poured into ice/water. The mixture was extracted with $CHCl_3$. The precipitate in the aqueous layer was filtered and the residue recrystallised from toluene to give **1**, a white powder (1.3 g, 11%). The organic layers were washed successively with water, $NaHCO_3$, water, combined, dried over Na_2SO_4, filtered and concentrated. The solid obtained was recrystallised from toluene to give **1**, a white powder (4.87 g, 43%).

Rf: EtOAc 1/hexane 1: 0.37
^{1}H NMR ($CDCl_3$, 400.13 MHz, 300 K) δ: 7.79 (d, 2H, J_{ortho} = 8.9 Hz), 7.75 (d, 2H, J_{ortho} = 8.7 Hz), 6.96 (d, 2H, J_{ortho} = 8.9 Hz), 6.90 (d, 2H, J_{ortho} = 8.7 Hz), 5.44 (s, 1H), 3.89 (s, 3H)

4-(3-Hydroxypropoxy)-phenyl-4'-methoxybenzophenone (2)

A suspension of 4-hydroxy-4'-methoxybenzophenone (**1**) (2.1 g, 9.20 mmol), 3-bromopropan-1-ol (1.2 mL, 13.27 mmol), potassium carbonate (2.1 g) and sodium iodide

(0.9 g) in butanone (30 mL) was stirred and heated at reflux for 48 hours. The mixture was filtered and the filtrate evaporated. The crude product obtained was recrystallised from ethanol to give a pale yellow solid, **2**, with a yield of 49% (1.28 g).

Rf: EtOAc 1/hexane 1: 0.20

^{1}H NMR ($CDCl_3$, 400.13 MHz, 300 K) δ: 7.79 (m, 4H), 6.98 (m, 4H), 4.21 (t, 2H, ^3J = 6.0 Hz), 3.90 (td, 2H, ^3J = 6.0 Hz, ^3J = 5.3 Hz), 3.89 (s, 3H), 2.09 (qt, 2H, ^3J = 6.0 Hz), 1.64 (t, 1H, ^3J = 5.3 Hz)

4,4'-Bis-[4-(3-hydroxypropoxy)]benzophenone (3)

Using the same procedure as for compound **2**. Chromatography (SiO_2: EtOAc). **3**: yield: 58%, pale yellow solid. By-product, **3a**, yield: 14%, white solid.

Rf: EtOAc: 0.24

^{1}H NMR (DMSO-d_6, 400.13 MHz, 300 K) δ: 7.75 (m, 4H), 7.13 (m, 4H), 4.66 (t, 2H, ^3J = 5.2 Hz), 4.20 (t, 4H, ^3J = 6.4 Hz), 3.63 (td, 4H, ^3J = 6.4 Hz, ^3J = 5.2 Hz), 1.95 (qt, 4H, ^3J = 6.4 Hz)

4-Hydroxy-4'-(3-hydroxypropoxy)benzophenone (3a)

Rf: EtOAc: 0.44

^{1}H NMR (DMSO-d_6, 400.13 MHz, 300 K) δ: 10.40 (s, 1H), 7.73 (dd, 2H, J_{ortho} = 6.9 Hz, J_{meta} = 2.0 Hz), 7.68 (dd, 2H, J_{ortho} = 6.8 Hz, J_{meta} = 1.9 Hz), 7.12 (dd, 2H, J_{ortho} = 6.9 Hz, J_{meta} = 2.0 Hz), 6.94 (dd, J_{ortho} = 6.8 Hz, J_{meta} = 1.9 Hz), 4.66 (t, 1H, ^3J = 6.3 Hz), 4.19 (t, 2H, ^3J = 6.3 Hz), 3.63 (td, 2H, ^3J = 6.3 Hz, ^3J = 6.3 Hz), 1.95 (qt, 2H, ^3J = 6.3 Hz)

4,4'-Bis-(acryloyloxy)benzophenone (4)

To a suspension of 4,4'-dihydroxybenzophenone (5.0 g, 23.34 mmol) in MeCN (230 mL) cooled to ≈ -10 °C, DBU (7.7 mL, 51.54 mmol) was added in a single portion. The solution was stirred for 20 minutes and then acryloylchloride (5.2 mL, 63.99 mmol) dissolved in MeCN (25 mL) was added dropwise to the mixture. The mixture was stirred until room temperature for 28 hours. MeCN was removed and then water and DCM were added. The aqueous layer was extracted with DCM. The organic layers were washed with a solution of HCl 2M, combined, dried over Na_2SO_4 and concentrated. The yellow solid obtained was chromatographied (SiO_2: EtOAc 3 / hexane 7) to deliver 0.95 g of **4**, a white solid (13%).

Rf: EtOAc 3 / hexane 7: 0.59

^{1}H NMR ($CDCl_3$, 400.13 MHz, 300 K) δ: 7.88 (m, 2H), 7.28 (m, 2H), 6.66 (dd, 1H, $^3J_{trans}$ = 17.2 Hz, $^2J_{gem}$ = 1.2 Hz), 6.35 (dd, $^3J_{trans}$ = 17.2 Hz, $^3J_{cis}$ = 10.4 Hz), 6.08 (dd, $^3J_{cis}$ = 10.4 Hz, $^2J_{gem}$ = 1.2 Hz)

4-[1-Hydroxy-1-(4-methoxyphenyl)prop-2-ynyl]phenol (5)

Under a nitrogen atmosphere, THF (60 mL) was cooled to -10 °C, then TMSacetylene (2.7 mL, 19.1 mmol) was added in a single portion and BuLi (12 mL,1.6M in hexane,19.2 mmol) was added dropwise. After 30 minutes stirring at –10 °C, (4-hydroxyphenyl)-(4-methoxyphenyl)methanone (**1**) (2.0 g, 8.8 mmol) was added and the mixture was stirred at room temperature for 22 hours. Then potassium hydroxide (1.0 g, 17.8 mmol) diluted in MeOH (2 mL) was added to the mixture which was cooled at 0 °C. Desilylation was completed within 45 minutes. Then, at the mixture cooled at 0 °C, acetic acid was added until a pH of 6. The mixture was poured in a solution of NH_4Cl and extracted with EtOAc. The organic layers were successively washed with water, a satured soltion of NaCl and water, combined, dried over Na_2SO_4, filtered and concentrated to give a dark brown oil, **5**, with a yield of 100 % (2.23 g).

Rf: EtOAc 1 / hexane 1: 0.50

^{1}H NMR ($CDCl_3$, 400.13 MHz, 300 K) δ: 7.49 (dd, 2H, J_{ortho} = 6.8 Hz, J_{meta} = 2.1 Hz), 7.45 (dd, 2H, J_{ortho} = 6.6 Hz, J_{meta} = 2.1 Hz), 6.86 (dd, 2H, J_{ortho} = 6.8 Hz, J_{meta} = 2.1 Hz), 6.79 (dd, 2H, J_{ortho} = 6.6 Hz, J_{meta} = 2.1 Hz), 3.80 (s, 3H), 2.86 (s, 1H), 2.72 (s, 1H)

1,1-Bis-[4-(3-hydroxypropoxy)phenyl]prop-2-yn-1-ol (6)

Using the same procedure as for compound **5**. **6**: yield: 100%, yellow oil.

Rf: EtOAc 1 / hexane 1: 0.25
^{1}H NMR ($CDCl_3$, 400.13 MHz, 300 K) δ: 7.49 (m, 4H), 6.86 (m, 4H), 4.11 (t, 2H, ^3J = 6.0 Hz), 3.85 (t, 2H, ^3J = 6.0 Hz), 3.80 (s, 3H), 2.86 (s, 1H), 2.73 (s, 1H), 2.03 (qt, 2H, ^3J = 6.0 Hz)

1-[4-(3-Hydroxypropoxy)phenyl]-1-(4-methoxyphenyl)prop-2-yn-1-ol (7)

Using the same procedure as for compound **5**. Chromatography (SiO_2: EtOAc). **7**: yield: 40%, yellow oil. By-product, **3**, pale yellow solid (starting material). Yield of **7**: 49%.

Rf: EtOAc: 0.39
^{1}H NMR ($CDCl_3$, 400.13 MHz, 300 K) δ: 7.49 (m, 4H), 6.86 (m, 4H), 4.13 (t, 4H, ^3J = 6.0 Hz), 3.86 (m, 4H), 2.86 (s, 1H), 2.70 (s, 1H), 2.05 (m, 4H), 1.69 (m, 2H)

3,3-Bis-(4-methoxyphenyl)-9-hydroxy-3*H*-naphtho[2,1-*b*]pyran (8)

A mixture of 2,7-dihydroxynaphthalene (6.0 g, 37.5 mmol) and 1,1-di-(4-methoxyphenyl)prop-2-yn-1-ol (10.0 g, 37.3 mmol) in toluene (600 mL) was heated at reflux for 45 minutes. Then alumina (20.0 g) was added and the mixture was heated at reflux for 4 hours. The mixture was filtered hot and the residue washed with EtOAc. The filtrate was evaporated and the residue suspended in hexane and 10 drops of EtOAc. The suspension was filtered. Further hexane and EtOAc were added to the solid under heating (100 °C), but the solid did not dissolved entirely. The mixture was heated in order to

concentrate it and then allowed to cool at room temperature. Then the mixture was filtered to give a pale brown solid, **8a** (3.33 g, 14%). The filtrate was concentrated and at the residue suspended in hexane and 10 drops of EtOAc. The suspension was filtered to give a red-brown solid, **8**, with a yield of 35% (5.38 g).

Rf: EtOAc 1 / hexane 1: 0.14

^{1}H NMR ($CDCl_3$, 400.13 MHz, 300 K) δ: 7.60 (d, 1H, J_{ortho} = 8.8 Hz), 7.56 (d, 1H, J_{ortho} = 8.8 Hz), 7.37 (m, 4H), 7.25 (d, 1H, J_{meta} = 2.4 Hz), 7.14 (d, 1H, ^{3}J = 10.0 Hz), 7.01 (d, 1H, J_{ortho} = 8.8 Hz), 6.90 (dd, 1H, J_{ortho} = 8.8 Hz, J_{meta} = 2.4 Hz), 6.83 (m, 4H), 6.17 (d, 1H, ^{3}J = 10.0 Hz), 4.99 (s, OH), 3.77 (s, 3H)

3,3,10,10-Tetrakis(4-methoxyphenyl)-3*H*,10*H*-naphtho[2,1-b:7,8-b']dipyran (8a)

Rf: EtOAc 1 / hexane 1: 0.26

^{1}H NMR ($CDCl_3$, 400.13 MHz, 300 K) δ: 7.49 (d, 2H, J_{ortho} = 8.8 Hz), 7.40 (m, 8H), 7.10 (d, 2H, J_{ortho} = 9.7 Hz), 7.00 (d, 2H, J_{ortho} = 8.8 Hz), 6.83 (m, 8H), 6.00 (d, 2H, J_{ortho} = 9.7 Hz), 3.77 (s, 6H)

3-(4-Hydroxyphenyl)-3-(4-methoxyphenyl)- 9-hydroxy-3*H*-naphtho[2,1-*b*]pyran (9)

Using the same procedure as for compound **8**. Chromatography (SiO_2: EtOAc 1/ hexane 1). **9**: yield: 70%, pink solid.

Rf: EtOAc 1/ hexane 1: 0.29

^{1}H NMR ($CDCl_3$, 400.13 MHz, 300 K) δ: 7.60 (d, 1H, J_{ortho} = 8.8 Hz), 7.56 (d, 1H, J_{ortho} = 8.4 Hz), 7.34 (m, 4H), 7.24 (d, 1H, J_{meta} = 2.4 Hz), 7.12 (d, 1H, ^{3}J = 10.0 Hz), 7.00 (d, 1H, J_{ortho} = 8.4 Hz), 6.90 (dd, 1H, J_{ortho} = 8.8 Hz, J_{meta} = 2.4 Hz), 6.83 (m, 2H), 6.75 (m, 2H), 6.15 (d, 1H, ^{3}J = 10.0 Hz), 5.16 (s, OH), 4.92 (s, OH), 3.77 (s, 3H)

3,3-Bis(4-methoxyphenyl)-9-(3-hydroxypropoxy)-3*H*-naphtho[2,1-*b*]pyran (10)

Using the same procedure as for compound **2**. Chromatography (SiO_2: EtOAc 1/ hexane 1). **10**: yield: 65%, orange solid.

Rf: EtOAc 1/ hexane 1: 0.23

^{1}H NMR ($CDCl_3$, 400.13 MHz, 300 K) δ: 7.60 (d, 1H, J_{ortho} = 8.9 Hz), 7.56 (d, 1H, J_{ortho} = 8.7 Hz), 7.38 (m, 4H), 7.25 (d, 1H, J_{meta} = 2.2 Hz), 7.19 (d, 1H, ^3J = 10.0 Hz), 7.02 (d, 1H, J_{ortho} = 8.7 Hz), 6.98 (dd, 1H, J_{ortho} = 8.9 Hz, J_{meta} = 2.2 Hz), 6.84 (m, 4H), 6.18 (d, 1H, ^3J = 10.0 Hz), 4.26 (t, 2H, ^3J = 6.0 Hz), 3.91 (td, 2H, ^3J = 6.0 Hz, ^3J = 6.0 Hz), 3.77 (s, 6H), 2.12 (qt, 2H, ^3J = 6.0 Hz)

7-Acetoxy-2-naphthol (11)

Using the procedure described in the literature by R. Lesser, E. Kranepuhl and G. Gad.[2] Yield of 42%. **11a** was obtained too with a yield of 12%.

Rf: EtOAc 1/ hexane 1: 0.42

^{1}H NMR (DMSO-d_6, 400.13 MHz, 300 K) δ: 9.86 (s, OH), 7.80 (d, 1H, J_{ortho} = 9.2 Hz), 7.78 (d, 1H, J_{ortho} = 9.2 Hz), 7.42 (dd, 1H, J_{meta} = 2.4 Hz), 7.10 (d, 1H, J_{meta} = 2.4 Hz), 7.07 (dd, 1H, J_{ortho} = 9.2 Hz, J_{meta} = 2.4 Hz), 7.03 (dd, 1H, J_{ortho} = 9.2 Hz, J_{meta} = 2.4 Hz), 2.31 (s, 3H)

2,7-diacetoxynaphthalene (11a)

Rf: EtOAc 1/ hexane 1: 0.52

^{1}H NMR ($CDCl_3$, 400.13 MHz, 300 K) δ: 7.85 (d, 2H, J_{ortho} = 8.9 Hz), 7.52 (d, 2H, J_{meta} = 2.2 Hz), 7.22 (dd, 2H, J_{ortho} = 8.9 Hz, J_{meta} = 2.2 Hz)

9-Acetoxy-[3,3-bis-(4-methoxyphenyl)]-3*H*-naphtho[2,1-*b*]pyran (12)

Using the same procedure as for compound **8**. Recrystallised in hexane/EtOAc to give a mixture of **12** (77%) and **8a** (23%).

9- Acryloyloxy -[3,3-bis-(4-methoxyphenyl)]-3*H*-naphtho[2,1-*b*]pyran (13)

Using the same procedure as for compound **4**. **13**: yield: 98%,orange solid.

Rf: EtOAc 3/ hexane 7: 0.24

^{1}H NMR ($CDCl_3$, 400.13 MHz, 300 K) δ: 7.73 (d, 1H, J_{ortho} = 8.8 Hz), 7.68 (d, 1H, J_{meta} = 2.0 Hz), 7.36 (m, 4H), 7.17 (d, 1H, ^3J = 10.0 Hz), 7.14 (d, 1H, J_{ortho} = 8.8 Hz), 7.09 (dd, 1H, J_{ortho} = 8.8 Hz, J_{meta} = 2.0 Hz), 6.84 (m, 4H), 6.65 (dd, 1H, $^3J_{trans}$ = 17.2 Hz, $^2J_{gem}$ = 1.2 Hz), 6.37 (dd, 1H, $^3J_{trans}$ = 17.2 Hz, $^3J_{cis}$ = 10.4 Hz), 6.19 (d, ^3J = 10.0 Hz), 6.05 (dd, $^3J_{cis}$ = 10.4 Hz, $^2J_{gem}$ = 1.2 Hz), 3.77 (s, 6H)

9-[3-(Acryloyloxy)propoxy]-3,3-bis(4-methoxyphenyl)-3*H*-naphtho[2,1-*b*]pyran(14)

Using the same procedure as for compound **4**. **14**: yield: 98%,orange oil.

Rf: EtOAc 1/ hexane 1: 0.63

^{1}H NMR ($CDCl_3$, 400.13 MHz, 300 K) δ: 7.60 (d, 1H, J_{ortho} = 8.8 Hz), 7.56 (d, 1H, J_{ortho} = 8.8 Hz), 7.38 (m, 4H), 7.21 (d, 1H, J_{meta} = 2.4 Hz), 7.20 (d, 1H, ^3J = 10.0 Hz), 7.02 (d, 1H, J_{ortho} = 8.8 Hz), 6.96 (dd, 1H, J_{ortho} = 9.0 Hz, J_{meta} = 2.4 Hz), 6.84 (m, 4H), 6.43 (dd, 1H, $^3J_{trans}$ = 17.2 Hz, $^2J_{gem}$ = 1.2 Hz), 6.19 (d, 1H, ^3J = 10.0 Hz), 6.14 (dd, 1H, $^3J_{trans}$ = 17.2 Hz, $^3J_{cis}$ = 10.4 Hz), 5.84 (dd, 1H, $^3J_{cis}$ = 10.4 Hz, $^2J_{gem}$ = 1.2 Hz), 4.40 (t, 2H, ^3J = 6.4 Hz), 4.19 (t, 2H, ^3J = 6.4 Hz), 3.77 (s, 6H), 2.23 (qt, 2H, ^3J = 6.4 Hz)

9-(Acryloyloxy)-3-(4-acryloyloxyphenyl)-3-(4-methoxyphenyl)-3*H*-naphtho[2,1-*b*]pyran (15)

Using the same procedure as for compound **4**. Chromatography (SiO_2: EtOAc 3/ hexane 7).

15: yield:23 %,pale yellow solid.

Rf: EtOAc 3/ hexane 7: 0.46

^{1}H NMR ($CDCl_3$, 400.13 MHz, 300 K) δ: 7.23 (d, 1H, J_{ortho} = 8.8 Hz), 7.69 (d, 1H, J_{meta} = 2.2 Hz), 7.65 (d, 1H, J_{ortho} = 8.8 Hz), 7.48 (m, 2H), 7.38 (m, 2H), 7.19 (d, 1H, ^3J = 9.6 Hz), 7.15 (d, 1H, J_{ortho} = 8.8 Hz), 7.10 (dd, 1H, J_{ortho} = 8.8 Hz, J_{meta} = 2.2 Hz), 7.09 (m, 2H), 6.84 (m, 2H), 6.65 (dd, 1H, $^3J_{trans}$ = 17.4 Hz, $^2J_{gem}$ = 1.2 Hz), 6.59 (dd, 1H, $^3J_{trans}$ = 17.4 Hz, $^2J_{gem}$ = 1.2 Hz), 6.37 (dd, 1H, $^3J_{trans}$ = 17.2 Hz, $^3J_{cis}$ = 10.4 Hz), (dd, 1H, $^3J_{trans}$ = 17.4 Hz, $^3J_{cis}$ = 10.4 Hz), 6.19 (d, 1H, ^3J = 9.6 Hz), 6.05 (dd, 1H, $^3J_{cis}$ = 10.4 Hz, $^2J_{gem}$ = 1.2 Hz), 6.01 (dd, 1H, $^3J_{cis}$ = 10.4 Hz, $^2J_{gem}$ = 1.2 Hz), 3.77 (s, 3H)

3,3-Bis-(4-methoxyphenyl)- 3*H*-naphtho[2,1-*b*]pyran (16)

Using the same procedure as for compound **8**. Recrystallised in hexane/EtOAc to give **16**, pale brown solid (59%).

Rf: EtOAc 3/ hexane 7: 0.36

^{1}H NMR ($CDCl_3$, 400.13 MHz, 300 K) δ: 7.95 (d, 1H, J_{ortho} = 8.4 Hz), 7.71 (d, 1H, J_{ortho} = 8.4 Hz), 7.64 (d, 1H, J_{ortho} = 8.8 Hz), 7.46 (m, 1H), 7.38 (m, 4H), 7.31 (m, 1H), 7.28 (d, 1H, ^3J = 10.0 Hz), 7.17 (d, 1H, J_{ortho} = 8.8 Hz), 6.84 (m, 4H), 6.21 (d, 1H, ^3J = 10.0 Hz), 3.77 (s, 6H)

3-(4-Hydroxyphenyl)-3-(4-methoxyphenyl)-3*H*-naphtho[2,1-*b*]pyran (17)

Using the same procedure as for compound **8**. Chromatography (SiO_2: EtOAc 3/ hexane 7).

17: yield: 37 %, pink powder.

Rf: EtOAc 3/ hexane 7: 0.36

^{1}H NMR ($CDCl_3$, 400.13 MHz, 300 K) δ: 7.95 (d, 1H, J_{ortho} = 8.4 Hz), 7.71 (d, 1H, J_{ortho} = 8.4 Hz), 7.64 (d, 1H, J_{ortho} = 8.8 Hz), 7.46 (m, 1H), 7.38 (m, 4H), 7.31 (m, 1H), 7.28 (d, 1H, ^3J = 10.0 Hz), 7.16 (d, 1H, J_{ortho} = 8.8 Hz), 6.84 (m, 2H), 6.76 (m, 2H), 6.19 (d, 1H, ^3J = 10.0 Hz), 4.82 (s, OH), 3.77 (s, 3H)

3-[4-(3-Hydroxypropxy)phenyl]-3-(4-methoxyphenyl)-3*H*-naphtho[2,1-*b*]pyran (18)

Using the same procedure as for compound **8**. Chromatography (SiO_2: EtOAc 1/ hexane 1).

18: yield: 71 %, red oil.

Rf: EtOAc 1/ hexane 1: 0.32

^{1}H NMR ($CDCl_3$, 400.13 MHz, 300 K) δ: 7.95 (d, 1H, J_{ortho} = 8.4 Hz), 7.71 (d, 1H, J_{ortho} = 8.4 Hz), 7.64 (d, 1H, J_{ortho} = 8.8 Hz), 7.46 (m, 1H), 7.38 (m, 4H), 7.31 (m, 1H), 7.29 (d, 1H, ^3J = 10.0 Hz), 7.16 (d, 1H, J_{ortho} = 8.8 Hz), 6.84 (m, 4H), 6.20 (d, 1H, ^3J = 10.0 Hz), 4.09 (t, 2H, ^3J = 5.6 Hz), 3.84 (td, 2H, ^3J = 5.6 Hz, ^3J = 5.6 Hz), 3.77 (s, 3H), 2.02 (qt, 2H, ^3J = 5.6 Hz), 1.69 (t, OH, ^{3}J = 5.6 Hz)

3,3-Bis[4-(3-hydroxypropoxy)-phenyl]- 3*H*-naphtho[2,1-*b*]pyran (19)

Using the same procedure as for compound **8**. Chromatography (SiO_2: EtOAc).

19: yield: 46 %, orange solid.

Rf: EtOAc: 0.36

^{1}H NMR ($CDCl_3$, 400.13 MHz, 300 K) δ: 7.95 (d, 1H, J_{ortho} = 8.4 Hz), 7.71 (d, 1H, J_{ortho} = 8.4 Hz), 7.64 (d, 1H, J_{ortho} = 8.8 Hz), 7.46 (m, 1H), 7.38 (m, 4H), 7.31 (m, 1H), 7.29 (d, 1H, ^3J = 10.0 Hz), 7.16 (d, 1H, J_{ortho} = 8.8 Hz), 6.84 (m, 4H), 6.19 (d, 1H, ^3J = 10.0 Hz), 4.09 (t, 4H, ^3J = 5.6 Hz), 3.8 (td, 4H, ^3J = 5.6 Hz), 2.02 (qt, 4H, ^3J = 5.6 Hz), 1.69 (t, OH, ^3J = 5.6 Hz)

3-(4-Acryloyloxyphenyl)-3-(4-methoxyphenyl)-3*H*-naphtho[2,1-*b*]pyran (20)

Using the same procedure as for compound **4**. Chromatography (SiO_2: EtOAc 3/ hexane 7).

20: yield: 41 %, orange solid.

Rf: EtOAc 1/ hexane 1: 0.65

^{1}H NMR ($CDCl_3$, 400.13 MHz, 300 K) δ: 7.96 (d, 1H, J_{ortho} = 8.4 Hz), 7.72 (d, 1H, J_{ortho} = 8.4 Hz), 7.65 (d, 1H, J_{ortho} = 8.8 Hz), 7.50 (m, 2H), 7.47 (m, 1H), 7.39 (m, 2H), 7.32 (m, 1H), 7.31 (d, 1H, ^3J = 10.0 Hz), 7.17 (d, 1H, J_{ortho} = 8.8 Hz), 7.09 (m, 2H), 6.84 (m, 2H), 6.58 (dd, 1H, $^3J_{trans}$ = 17.2 Hz, $^2J_{gem}$ = 1.2 Hz), 6.30 (dd, 1H, $^3J_{trans}$ = 17.2 Hz, $^3J_{cis}$ = 10.4 Hz), 6.21 (d, 1H, ^3J = 10.0 Hz), 6.01 (dd, 1H, $^3J_{cis}$ = 10.4 Hz, $^2J_{gem}$ = 1.2 Hz), 3.77 (s, 3H)

3-[4-(3-Acryloyloxypropoxy)phenyl]-3-(4-methoxyphenyl)- 3*H*-naphtho[2,1-*b*]pyran (21)

Using the same procedure as for compound **4**. Chromatography (SiO_2: EtOAc 3/ hexane 7).

21: yield: 60 %, red oil.

Rf: EtOAc 1/ hexane 1: 0.80

^{1}H NMR ($CDCl_3$, 400.13 MHz, 300 K) δ: 7.95 (d, 1H, J_{ortho} = 8.4 Hz), 7.71 (d, 1H, J_{ortho} = 8.4 Hz), 7.64 (d, 1H, J_{ortho} = 8.8 Hz), 7.46 (m, 1H), 7.38 (m, 4H), 7.31 (m, 1H), 7.28 (d, 1H, ^3J = 10.0 Hz), 7.16 (d, 1H, J_{ortho} = 8.8 Hz), 6.83 (m, 4H), 6.39 (dd, 1H, $^3J_{trans}$ = 17.2 Hz, $^2J_{gem}$ = 1.2 Hz), 6.20 (d, 1H, ^3J = 10.0 Hz), 6.10 (dd, 1H, $^3J_{trans}$ = 17.2 Hz, $^3J_{cis}$ = 10.4 Hz), 5.81 (dd, 1H, $^3J_{cis}$ = 10.4 Hz, $^2J_{gem}$ = 1.2 Hz), 4.33 (t, 2H, ^3J = 6.4 Hz), 4.03 (t, 2H, ^3J = 6.4 Hz), 3.77 (s, 3H), 2.13 (qt, 2H, ^3J = 6.4 Hz)

3,3-Bis-[4-(3-Acryloyloxypropoxy)phenyl]-3*H*-naphtho[2,1-*b*]pyran (22)

Using the same procedure as for compound **4**. Chromatography (SiO_2: EtOAc 3/ hexane 7).

22: yield: 53 %, pink oil.

Rf: EtOAc 3/ hexane 7: 0.49

^{1}H NMR ($CDCl_3$, 400.13 MHz, 300 K) δ: 7.95 (d, 1H, J_{ortho} = 8.4 Hz), 7.71 (d, 1H, J_{ortho} = 8.4 Hz), 7.64 (d, 1H, J_{ortho} = 8.8 Hz), 7.46 (m, 1H), 7.37 (m, 4H), 7.30 (m, 2H), 7.28 (d, 1H, ^{3}J = 10.0 Hz), 7.16 (d, 1H, J_{ortho} = 8.8 Hz), 6.83 (m, 4H), 6.39 (dd, 2H, $^{3}J_{trans}$ = 17.4 Hz, $^{2}J_{gem}$ = 1.2 Hz), 6.19 (d, 1H, ^{3}J = 10.0 Hz), 6.10 (dd, 2H, $^{3}J_{trans}$ = 17.4 Hz, $^{3}J_{cis}$ = 10.4 Hz), 5.81 (dd, 2H, $^{3}J_{cis}$ = 10.4 Hz, $^{2}J_{gem}$ = 1.2 Hz), 4.33 (t, 4H, ^{3}J = 6.4 Hz), 4.03 (t, 4H, ^{3}J = 6.4 Hz), 2.13 (qt, 4H, ^{3}J = 6.4 Hz)

4,4'-Bis(benzyloxy)benzophenone (23)

Using the procedure described in the literature by C. Kaiser and al.[3] Yield of 98%.

Rf: EtOAc 1/ hexane 1: 0.76

^{1}H NMR ($CDCL_3$, 400.13 MHz, 300 K) δ: 7.79 (m, 4H), 7.40 (m, 10H), 7.04 (m, 4H), 5.15 (s, 4H)

1,1-Bis-(4-benzyloxyphenyl)prop-2-yn-1-ol (24)

Using the same procedure as for compound **5**. **24**: yield: 100%, yellow oil.

Rf: EtOAc 1/ hexane 1: 0.62

^{1}H NMR ($CDCL_3$, 400.13 MHz, 300 K) δ: 7.49 (m, 4H), 7.37 (m, 10H), 6.93 (m, 4H), 5.05 (s, 4H), 2.85 (s, 1H), 2.70 (s, 1H)

3,3-Bis-(4-benzyloxyphenyl)-3*H*-naphtho[2,1-*b*]pyran (25)

Using the same procedure as for compound **8**. **25**: yield: 100 %, brown solid.

Rf: EtOAc 1/ hexane 1: 0.75

^{1}H NMR ($CDCl_3$, 400.13 MHz, 300 K) δ: 7.95 (d, 1H, J_{ortho} = 8.00 Hz), 7.70 (d, 1H, J_{ortho} = 8.0 Hz), 7.64 (d, 1H, J_{ortho} = 8.8 Hz), 7.48-7.15 (m, 14H), 6.91 (m, 4H), 6.20 (d, 1H, ^{3}J = 9.6 Hz), 5.02 (s, 4H)

Typical copolymerization procedure: Copolymerization of MMA with 9-acryloyloxy -[3,3-bis-(4-methoxyphenyl)]-3*H*-naphtho[2,1-*b*]pyran (13) in toluene. Methyl methacrylate (MMA; 2.1510 g, 21.5 mmol), **1** (0.0992 g, 0.214 mmol), 2-(2-cyanoisopropyl dithiobenzoate) (CPDB; 0.0471 g, 0.215 mmol), α,α'-azoisobutyronitrile (AIBN; 0.0175 g, 0.107 mmol) and toluene (1.9789 g) were mixed in a Schlenk tube. Prior to sealing, the mixture was carefully degassed by five freeze-pump-thaw cycles under high vacuum. The reaction was then heated at 60°C and samples were taken at various time and quenched in ice. Conversions were calculated via ^{1}H NMR and molecular weight distributions were analysed via SEC.

References

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