Design and photoinduced surface relief grating formation of photoresponsive azobenzene based molecular materials with ruthenium acetylides †

Gherab, Kichou N.; Gatri, Rafik; Hank, Zakia; Dick, Bernhard; Kutta, Roger-Jan; Winter, Rainer; Luc, Jérôme; Sahraoui, Bouchta; and Fillaut, Jean-Luc.

Supporting Information contains: Full preparation procedures and characterization of compounds **1a-c**, **2** and **3a**, **b**.

Preparation procedures and characterization of compounds 1a-c, 2 and 3a,b.

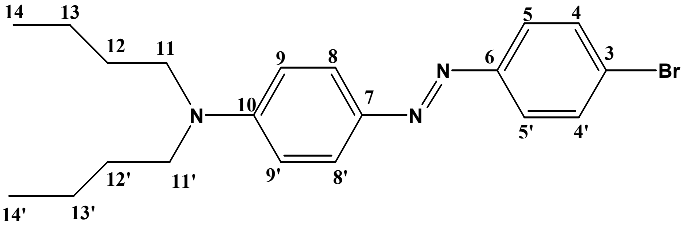
Experimental procedures

Moisture or oxygen sensitive reactions were performed under an inert atmosphere using standard Schlenk techniques with a double manifold vacuum line. Solvents were freed of impurities by usual procedures and stored under argon.

Materials. All reactions were performed under a nitrogen atmosphere with the use of Schlenk techniques unless stated otherwise. Dichloromethane, pentane and triethylamine were dried by distilling over calcium hydride; tetrahydrofuran and diethyl ether over sodium/benzophenone; pentane, toluene over sodium. Chromatography was performed on silica gel SiO_2 60 (ACROS 0.063-0.200 mm) and aluminium oxide (ACROS Al_2O_3 activated neutral 0.050-0.200 mm). Filtration was performed using Celite® 521 as filtering agent. Commercial reagents with purity > 98% were used directly. The following compounds were prepared by literature procedures: $[(dppe)_2RuCl]TfO$,[1, 2] 4-ethynylbenzaldehyde,[3] 1,4-ethynyl-thiophene carbaldehyde.[4]

Methods and Instrumentation. Secondary ion (SI) mass spectra were recorded on a VG ZAB 2SEQ spectrometer (30 kV Cs^+ ions, current 1 mA, accelerating potential 8 kV, matrix *o*-nitrophenyloctyl ether or *m*-nitrobenzylic alcohol) and electron impact (EI), including high-resolution (HR), mass spectra on a VG Autospec instrument (70 eV electron energy, 8 kV accelerating potential) at the Centre de Mesures Physiques de l'Ouest, Rennes, France. Microanalyses were carried out at the Centre de Mesures Physiques de l'Ouest, Rennes, France. UV-visible spectra were recorded in quartz cuvettes of pathlength 1 cm, using a Biotek Instruments Uvikon XS spectrometer. The efficacy of photoinduced *trans→cis* isomerization and the rate of thermal *cis→trans* back reisomerization were probed by irradiating μmolar cyclohexane solutions of the respective molecules (ca. 0.3 optical density) for 1s with 2 LEDs (Luxeon® III Emitter royal blue LXHL-PR09, Lumileds Lighting, San Jose, USA) with each of a radiometric power of 150 mW operating at 460 nm, close to the absorption maximum of the *trans*-isomers. Routine NMR spectra were recorded using a Bruker AC300P spectrometer or a Bruker DPX 200, respectively at 300.13 MHz or 200.13 MHz for ^{1}H, 75.48 MHz or 50.32 MHz for ^{13}C and 121.50 MHz or 81.01 MHz for ^{31}P. ^{1}H, ^{13}C and ^{31}P NMR spectra are referenced to residual chloroform (7.26 ppm; 77.16 ppm) or external H_3PO_4 (0.0 ppm), respectively. Dried powders were analysed by thermo-gravimetric analysis, TGA (Perkin-Elmer TGA7) at Institute of Physical and Theoretical Chemistry, University of Regensburg, Regensburg, Germany. TGA was performed from 25 to 600 C at a heating rate of 10 C/min in a nitrogen atmosphere. Differential scanning calorimetry was carried out on a Mettler DSC 30 (Institute of Physical and Theoretical Chemistry, University of Regensburg, Regensburg, Germany) under nitrogen atmosphere. The glass transition temperatures were determined from the DSC thermograms.

(E)-4-((4-bromophenyl)diazenyl)-N,N-dibutylbenzenamine (1.a)



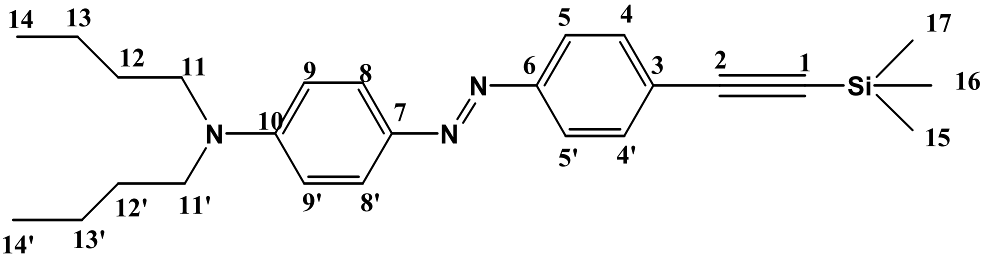
In a round bottom flask of 1l, bromoaniline (4 g, 23.2 mmol) is dissolved in 70 ml water. The solution is cooled to - 4°C and 7ml of concentrated HCl is added. In an Erlenmeyer (50 ml), sodium nitrite is dissolved in water (18ml) and cooled to -4° C. This solution is added to the bromoaniline solution. In a second Erlenmeyer, sodium acetate and N, N –dibutylaniline are dissolved in a mixture of ethanol: water (100:40). This solution is also cooled down to -4° C and added after 20 minutes to bromoaniline solution. The reaction mixture is stirred overnight at r.t. The saturated solution $NaHCO_3$ (20 ml) and dichloromethane (100 ml) is added to this mixture. Organic phase is extracted, dried over $MgSO_4$ and dried. The first purification is done by chromatography over silica gel with dichloromethane as solvent. Second purification is done by distillation under reduced pressure (110° C, 3mm Hg). 6.2 g of **1.a** was afforded as a red solid (68%).

^{1}H NMR ($CDCl_3$, 300.133 MHz, 297 K, δ ppm): 7.89 (d, $^3J_{HH}$ = 9.0Hz, 2H, $H_{8,8'}$), 7.72 (d, $^3J_{HH}$ = 8.7 Hz, 2H, $H_{5,5'}$), 7.63 (d, $^3J_{HH}$ = 8.7Hz, 2H, $H_{4,4'}$), 6.67 (d, $^3J_{HH}$ = 9.0Hz, 2H, $H_{9,9'}$), 3.42 (t, $^3J_{HH}$ =7.4 Hz, 4H, $H_{11,11'}$), 1.72-1.59 (m, 4H, $H_{12,12'}$), 1.41 (st, $^3J_{HH}$ =7.9 Hz, 4H, $H_{13,13'}$), 1.03 (t, $^3J_{HH}$ = 7.4 Hz, 6H, $H_{14,14'}$).

^{13}C{1H} NMR ($CDCl_3$, 50 MHz, 297 K, δ ppm): 152.1 (C_{10}), 150.8 (C_6), 142.9 (C_7), 132.1 ($C_{4,4'}$), 125.4 ($C_{5,5'}$), 123.7 ($C_{8,8'}$), 123 (C_3), 111.1 ($C_{9,9'}$), 51.0 ($C_{11,11'}$), 29.5 ($C_{12,12'}$), 20.3 ($C_{13,13'}$), 14.0 ($C_{14,14'}$).

Elemental Analysis: $C_{20}H_{26}BrN_3$: calcd: C 61.86, H 6.71, N 10.82; found: C 61.86, H 6.70, N 10.69.

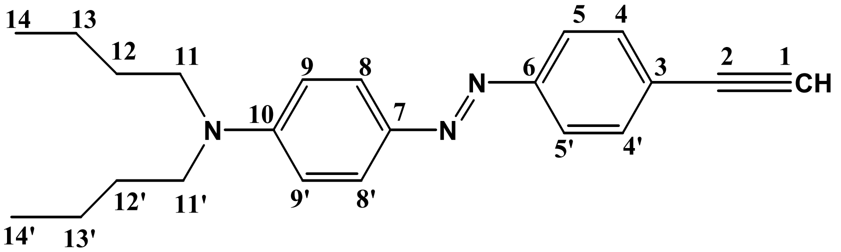
(E)-N, N-dibutyl-4-((4-((trimethylsilyl)ethynyl)phenyl)diazenyl)benzenamine (1.b)



In a Schlenk tube solution of **1.a** (100 mg, 0.25 mmol) in 10 ml of distilled THF and 10 ml of triethylamine were introduced under argon. TMSA (50 µl, 0.34 mmol), was then added along with 20 mg (0.029 mmol) of $PdCl_2(PPh_3)_2$ and 2 mg (0.01 mmol) of CuI. The reaction mixture was stirred for 20 hours at reflux. Then THF was removed under vacuum. The reaction mixture was extracted with diethyl ether Then product was purified on a silica gel column chromatography (eluent: pentane/diethyl ether 98:2) and was afforded as a red brownish solid (70 mg) in 67% yield.

^{1}H NMR ($CDCl_3$, 300.133 MHz, 297 K, δ ppm): 7.86 (d, $^{3}J_{HH}$ = 9.1 Hz, 2H, $H_{8,8'}$), 7.48 (d, 2H, $H_{5,5'}$), 7.61 (d, ,2H, $H_{4,4'}$), 6.70 (d , 2H, $H_{9,9'}$), 3.32 (t, ,4H, $H_{11,11'}$), 1.62 (m,4H, $H_{12,12'}$), 1.41 (m, 4H, $H_{13,13'}$), 1.19 (t, 6H, $H_{14,14'}$), 0.32 (s, 9H, $H_{15.16,17}$).
^{13}C {1H} NMR ($CDCl_3$, 50 MHz, 297 K, δ ppm): 150.8 (C_6), 149.1 (C_{10}),143.3 (C_7), 132.8 ($C_{4,4'}$), 125.6 ($C_{8,8'}$), 123.6 (C_3), 122.2 ($C_{5,5'}$), 111.2 ($C_{9,9'}$), 105.4.0 (C_2), 95.8 (C_1), 51.0 ($C_{11,11'}$), 29.6 ($C_{12,12'}$), 20.4 ($C_{13,13'}$), 14.1 ($C_{14,14'}$), 0.2 ($C_{15,16,17}$).
Mass spectrum: m/z $[M]^+$ calc. for $C_{25}H_{35}N_3Si$ calculated 405.26003, Found: 405.2597.
Elemental Analysis: $C_{25}H_{35}N_3Si$: calcd: C 74.02, H 8.70, N 10.36; found: C 74.36, H 8.61, N 10.39.

(E)-N, N-dibutyl-4-((4-ethynylphenyl)diazenyl)benzenamine 1c



In a Schlenk tube under argon (210 mg, 0.52 mmol) of **1.b** and solution of 1.1 equivalent of 1M Bu_4NF in distilled THF is added. The reaction mixture was stirred for 30 minutes at r.t. Then water was added and the mixture was extracted with diethyl ether. The mixture was dried (Na_2SO_4) and evaporated under vacuum. **1.c** was purified on a silica gel and column chromatography (eluent: pentane/diethyl ether 98:2) and was afforded as a red solid (172.80 mg) in 92% yield.

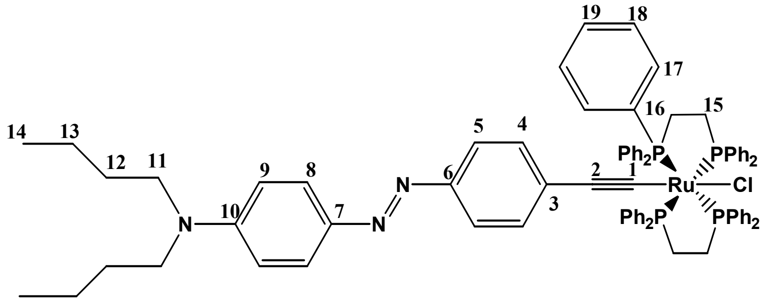
^{1}H NMR ($CDCl_3$, 300.133 MHz, 297 K, δ ppm): 7.84 (d, $^3J_{HH}$ = 9.0 Hz, 2H, $H_{8,8'}$), 7.72 (d, $^3J_{HH}$ = 8.4 Hz, 2H, $H_{5,5'}$), 7.63 (d, $^3J_{HH}$ =8.4 Hz, 2H, $H_{4,4'}$), 6.73 (d, $^3J_{HH}$ =9.0 Hz, 2H, $H_{9,9'}$), 3.28 (t, $^3J_{HH}$ =7.8 Hz, 4H, $H_{11,11'}$), 3.10 (s, 1H, H_1), 1.72-1.60 (m,4H, $H_{12,12'}$), 1.42 (m, 4H, $H_{13,13'}$), 1.03 (t, $^3J_{HH}$ = 7.1 Hz, 6H, $H_{14,14'}$).

^{13}C{1H} NMR ($CDCl_3$, 50 MHz, 297 K, δ ppm): 150.9 (C_6), 149.1 (C_{10}), 143.2 (C_7), 132.9 ($C_{4,4'}$), 125.6 ($C_{8,8'}$), 122.5 (C_3), 122.2 ($C_{5,5'}$), 111.6 ($C_{9,9'}$), 83.9 (C_2), 78.6 (C_1) 51.0 ($C_{11,11'}$), 29.6 ($C_{12,12'}$), 20.4 ($C_{13,13'}$), 14.1 ($C_{14,14'}$).

Mass spectrum: m/z $[M]^+$ calc. for $C_{22}H_{27}N_3$ calculated 333.22050, Found: 333.2192.

Elemental Analysis: $C_{22}H_{27}N_3$: calcd: C 79.24, H 8.16, N 12.60; found: C 79.86, H 8.10, N 12.39.

. **2**



In a Schlenk tube (0.092 mmol, 100 mg) of [(dppe)$_2$RuCl,TfO] and (61.27 mg, 0.18 mmol) of **1.c** were introduced under argon and dissolved in 10 ml of freshly distilled and degassed dichloromethane. The resulting mixture was stirred at r.t overnight. The completion of the reaction was monitored by ^{31}P NMR spectrometry (s, 38.9 ppm). The solvent was removed under reduced pressure and the dried product was washed several times with diethyl ether. Then product was taken in a Schlenk tube and dissolved in 10 ml of freshly distilled and degassed dichloromethane and deprotonated upon addition of NEt$_3$. Then the product was purified on a silica gel column chromatography (eluent: diethyl ether/THF 100:0 to 80:20), Compound **2** was afforded as a dark orange solid (100 mg) with 77 % yield.

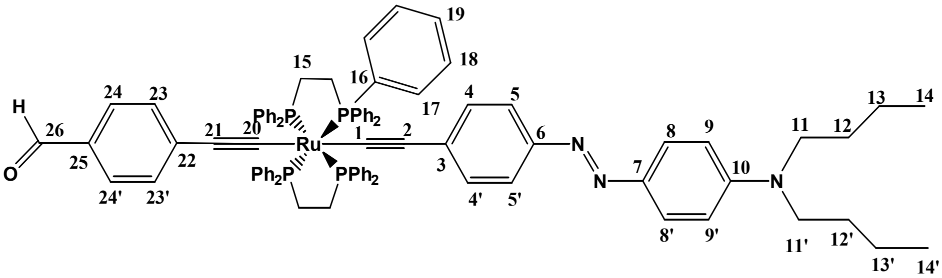
^{1}H NMR (CDCl$_3$, 300.133 MHz, 297 K, δppm): 7.78 (d, $^3J_{HH}$ = 8.5 Hz, 2H, $H_{8,8'}$), 7.67 (d, $^3J_{HH}$ = 7.9 Hz, 2H, $H_{5,5'}$) 7.62-6.78 (m, 40H of aromatics +$H_{4\text{-}4'}$, $H_{9,9'}$), 3.31 (t, $^3J_{HH}$ =8.2 Hz, 4H, $H_{11,11'}$), 1.72-1.56 (m, 4H, $H_{12,12'}$), 1.40 (m, 4H, $H_{13,13'}$), 2.80 (m, 8H, CH$_2$ dppe), 1.03 (t, $^3J_{HH}$ = 4.7 Hz, 6H, $H_{14,14'}$).

^{13}C {1H} NMR (CDCl$_3$, 125 MHz, 297 K, δppm): 150.0 (C_{10}), 149.0 (C_6), 143.6 (C_7), 132.5 (C_1, $|^2J_{P\text{-}C}|$ = 14.9 Hz), 136.3 (qt, $|^1J_{P\text{-}C} + {}^3J_{P\text{-}C}|$ = 12 Hz, Cq, C*ipso* dppe phenyl), 135.7 (qt, $|^1J_{P\text{-}C} + {}^3J_{P\text{-}C}|$ = 10 Hz, Cq, C*ipso* dppe phenyl), 134.5 (CH dppe phenyl), 134.2, 131.8 (C_3), 130.05 ($C_{4,4'}$), 124.7 ($C_{8,8'}$), 121.8 ($C_{5,5'}$), 115.7 (C_2), 111.2 ($C_{9,9'}$), 51.0 ($C_{11,11'}$), 30.7 (C_{15}, |qt, $^1J_{P\text{-}C} - {}^3J_{P\text{-}C}|$ = 23 Hz), 29.6 ($C_{12,12'}$), 20.0 ($C_{13,13'}$), 14.1 ($C_{14,14'}$).

^{31}P {^{1}H} NMR (CDCl$_3$, 81 MHz 297K, δppm): 49.2 (s).

Elemental Analysis: $C_{74}H_{74}N_3ClP_4Ru$ (1265.84): calcd: C 70.22, H 5.89, N 3.32; found: C 69.86, H 6.10, N 3.39.

(3a)



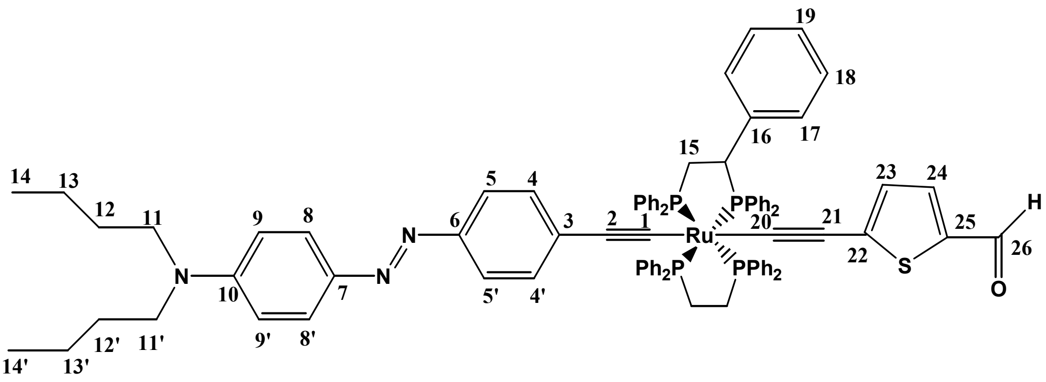
^{1}H NMR (CDCl$_3$, 300.133 MHz, 297 K, δ ppm): 9.89 (s, 1H, CHO), 7.91 (d, $^3J_{HH}$ = 8.9 Hz, 2H, H$_{8,8'}$), 7.78-6.81 (m, 40H of aromatics + H$_{5,5'}$, H$_{4\text{-}4'}$, H$_{9,9'}$, H$_{23,23'}$, H$_{24,24'}$), 3.28 (t, $^3J_{HH}$ =7.1 Hz, 4H, H$_{11,11'}$), 1.69-1.62 (m, 4H, H$_{12,12'}$), 1.41 (m, 4H, H$_{13,13'}$), 2.23 (m, 8 H, H$_{15}$),1.02 (t, $^3J_{HH}$ = 4.7 Hz, 6H, H$_{14,14'}$).

^{13}C{1H} NMR (CDCl$_3$, 125 MHz, 297 K, δ ppm): 191.3 (C$_{26}$), 150.0 (C$_{10}$), 149.3 (C$_6$), 148.3 (q, $^2J_{\text{p-c}}$ = 18.7 Hz), 143.5 (C$_7$), 136.8 (qt, $|^1J_{\text{P-C}} + {}^3J_{\text{P-C}}|$ = 11 Hz, Cq, Cipso dppe phenyl), 136.7 (qt, $|^1J_{\text{P-C}} + {}^3J_{\text{P-C}}|$ = 10 Hz, Cq, Cipso dppe phenyl), 134.2 (CH dppe phenyl), 134.1 (CH dppe phenyl), 137.0 (C$_{22}$), 131.8 (C$_3$), 131.1(C$_{25}$), 130.2 (C$_{23',\ 23'}$), 129.5 (C$_{24,24'}$), 124.8 (C$_{8,8'}$), 122.1 (C$_{21}$), 121.4 (C$_{5,\ 5'}$), 119.2 (C$_2$), 111.1 (C$_{9,9'}$), 110.4 (C$_{4,4'}$), 51.0 (C$_{11,11'}$),), 29.5 (C$_{12,12'}$), 20.3 (C$_{13,13'}$), 14.1 (C$_{14,14'}$)

^{31}P{^{1}H} NMR (CDCl$_3$, 81 MHz ,297K, δ ppm): 54.5 (s)

Elemental Analysis: $C_{83}H_{79}N_3OP_4Ru$ (1359.53): calcd: C 73.33, H 5.86, N 3.09; found: C 73.36, H 6.13, N 3.41.

(3b)



^1H NMR ($CDCl_3$, 300.133 MHz, 297 K, δ ppm): 9.89 (s, 1H, CHO) 7.90 (d, $^3J_{HH}$ = 8.9 Hz, 2H, $H_{8,8'}$), 7.78 - 6.80 (m, 40H of aromatics + $H_{5,5'}$, $H_{4-4'}$, $H_{9,9'}$, $H_{23,24}$) 3.29 (t, $^3J_{HH}$ =7.1 Hz, 4H, $H_{11,11'}$), 1.70 - 1.58 (m,4H, $H_{12,12'}$), 1.40 (m, 4H, $H_{13,13'}$), 2.22 (m, 8 H, CH_2 dppe), 1.04 (t, $^3J_{HH}$ = 4.7 Hz, 6H, $H_{14,14'}$).

^{13}C {1H} NMR ($CDCl_3$, 125 MHz, 297 K, δ ppm):. 191.5 (C_{26}), 150.1 (C_{10}), 149.4 (C_6), 148.3 (q,$^2J_{p-c}$= 18.7 Hz), 143.5, 136.8 (qt, $|^1J_{P-C} + {}^3J_{P-C}|$ = 11 Hz, Cq, C*ipso* dppe phenyl), 136.7 (qt, $|^1J_{P-C} + {}^3J_{P-C}|$ = 10 Hz, Cq, C*ipso* dppe phenyl), 143.5 (C_7), 142.1 (C_{25}), 137.0 (C_{22}), 134.3 (C_{24}), 130.4 (C_4), 126.6 (C_{23}), 124.8 (C_8), 121.9 (C_5), 113.6 (C_3), 111.9 (C_{21}), 111.2 (C_9), 51.0 (C_{11}), 31.4 (C_{15}) $|^1J_{P-C} - {}^3J_{P-C}|$ = 11.9 Hz, 29.6 (C_{12}), 20.4 (C_{13}), 14.1 (C_{14}).. ***^{31}P {^1H} NMR ($CDCl_3$, 81 MHz ,297K, δ ppm):*** 54.1 (s)

Elemental Analysis: $C_{81}H_{77}N_3O_1P_4SRu$ (1365.56): calcd: C 71.25, H 5.68, N 3.08, S 2.35; found: C 70.73, H 5.77, N 3.06, S 2.29.

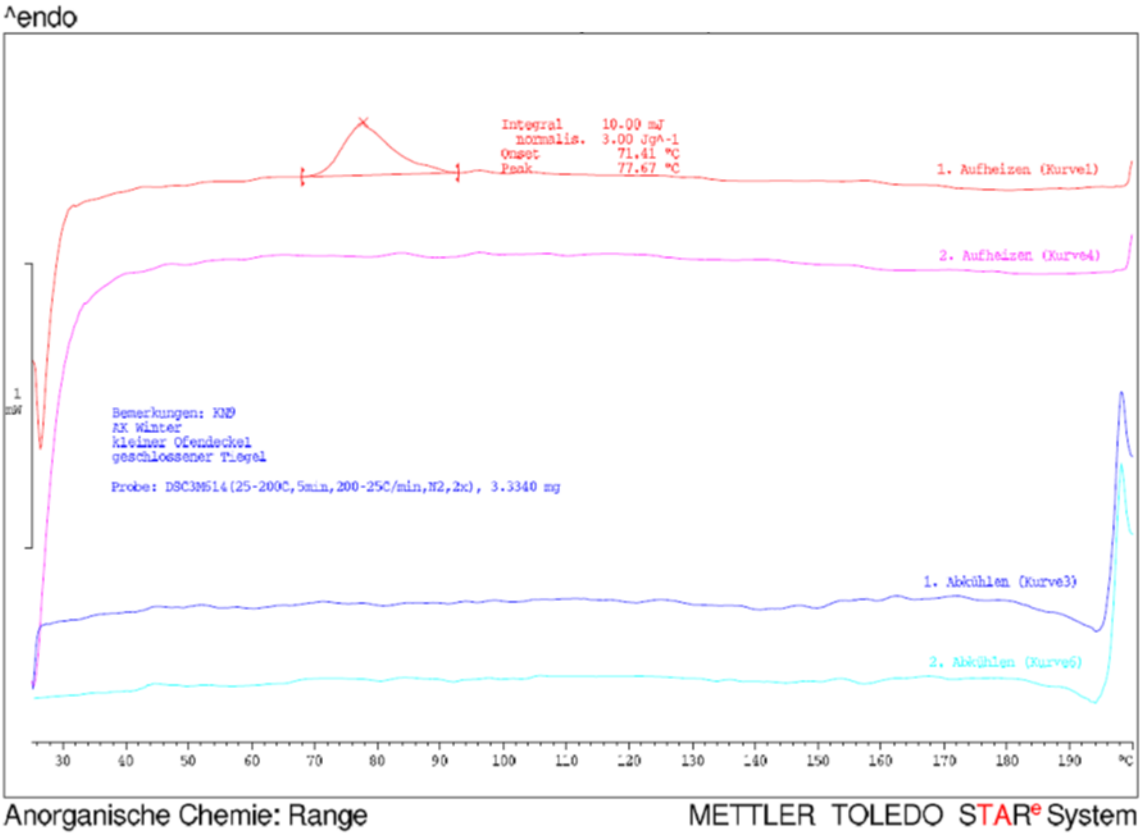


Figure S1: DSC curve of the complex **3a**.

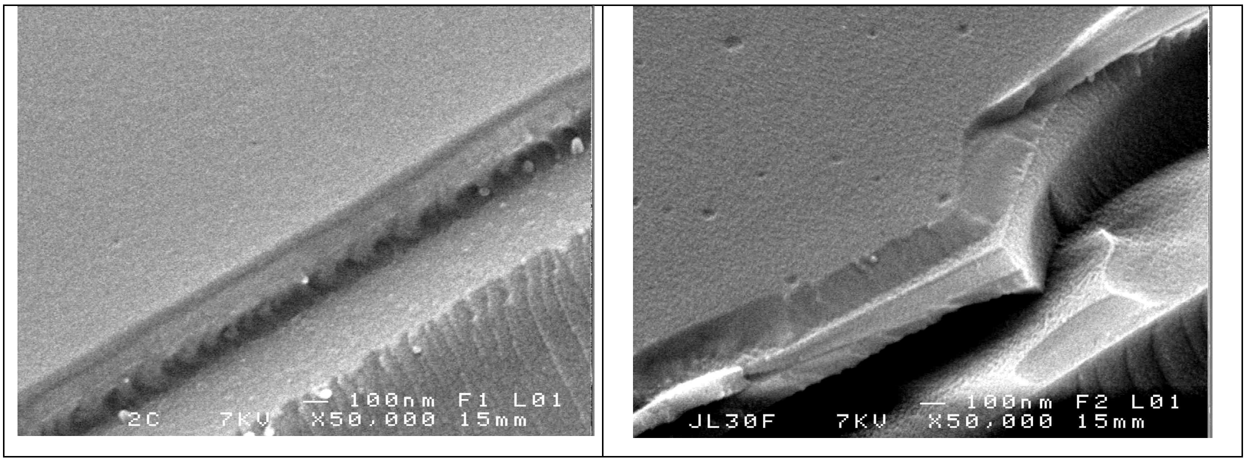


Figure S2. SEM Images of spin coated thin films of **2** (left superior corner), on a glass substrate.

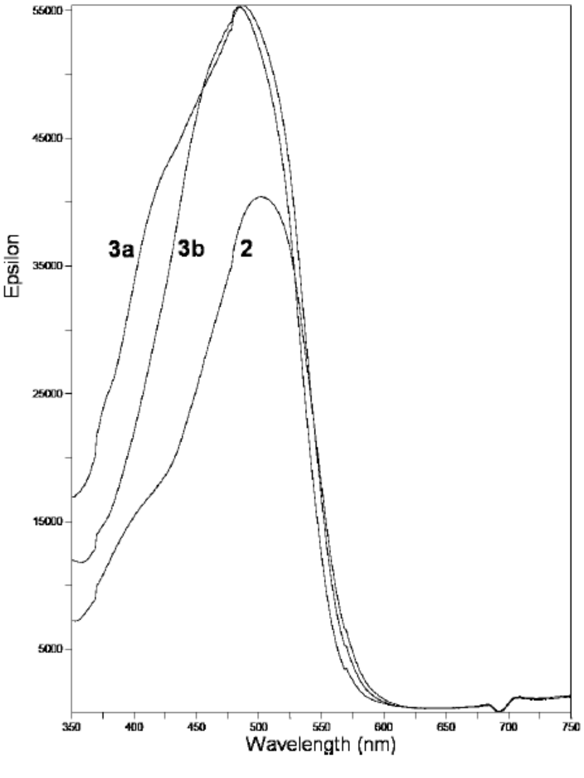


Figure S3. UV-NIR absorption spectra of **2\3a\3b** 10^{-5}M dichloromethane solutions.

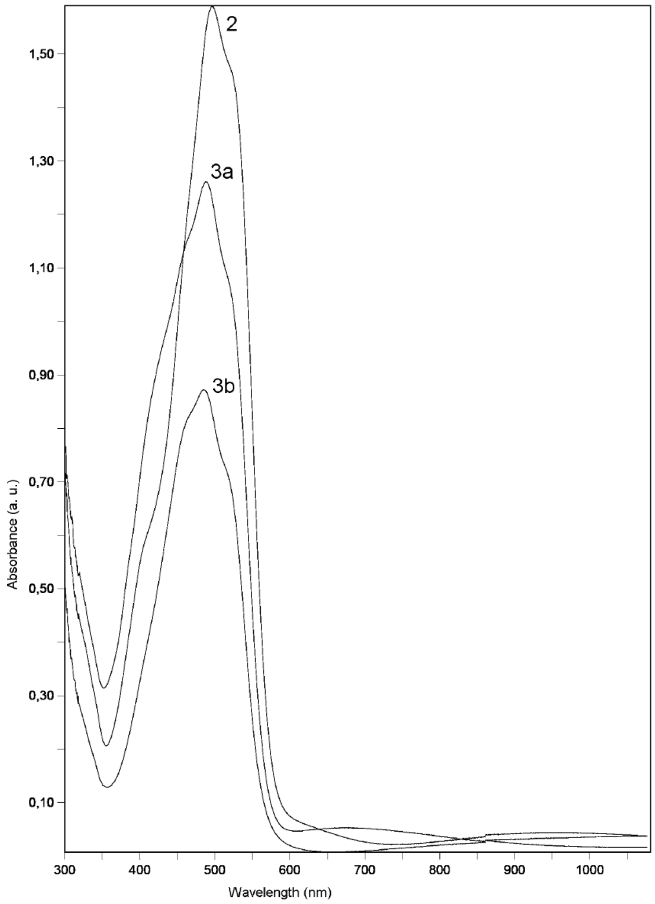


Figure S4. UV-NIR absorption spectra of **2\3a\3b** thin films.

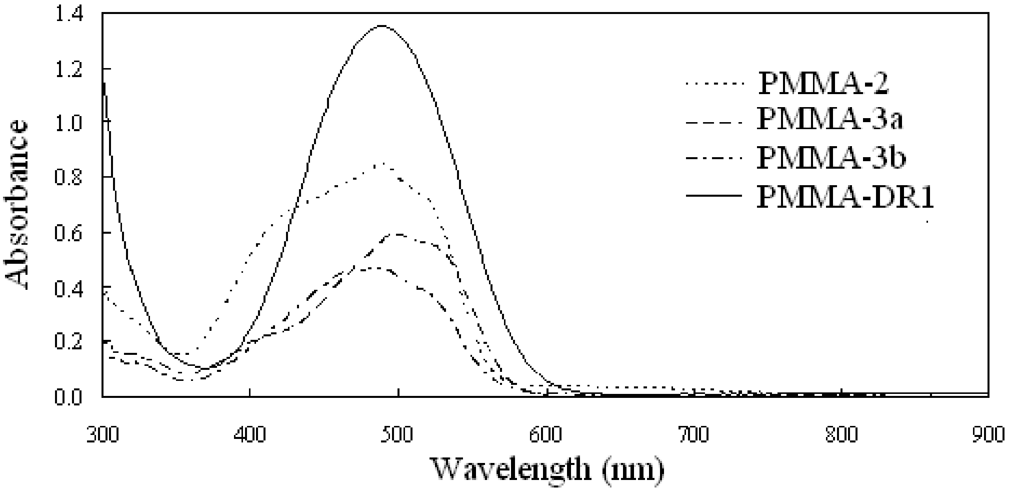


Figure S5: UV-NIR absorption spectra of doped **PMMA-2\3a\3b** and **PMMA-DR1** thin films.

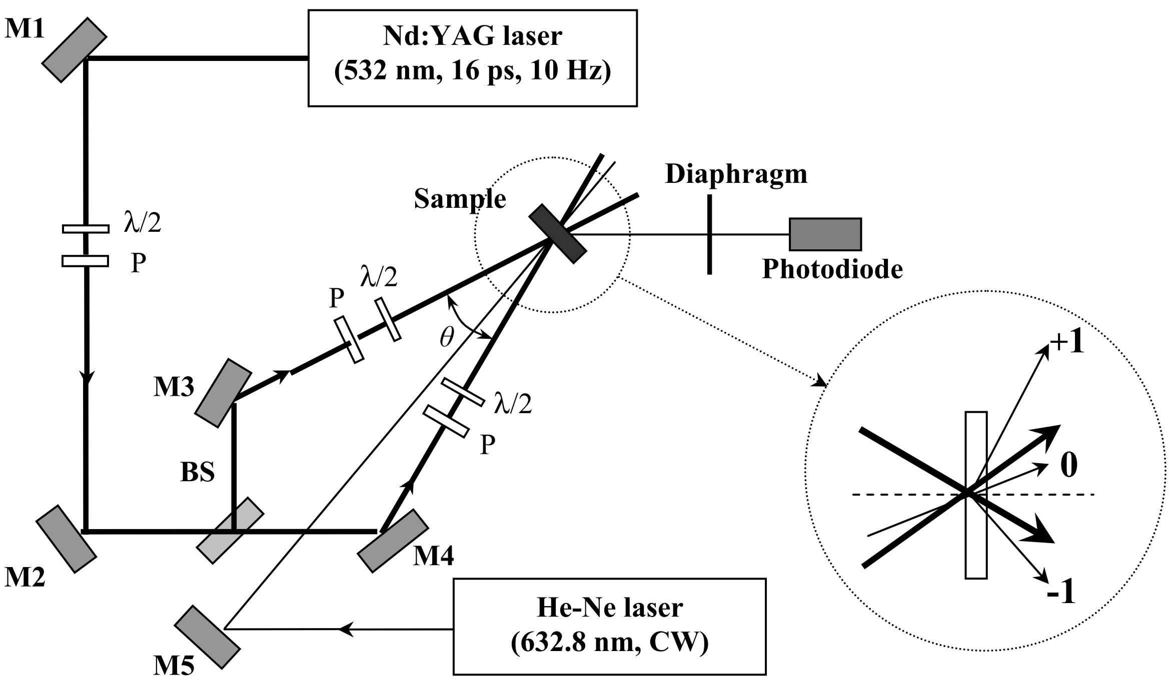


Figure S6. Experimental setup for surface relief grating formation.

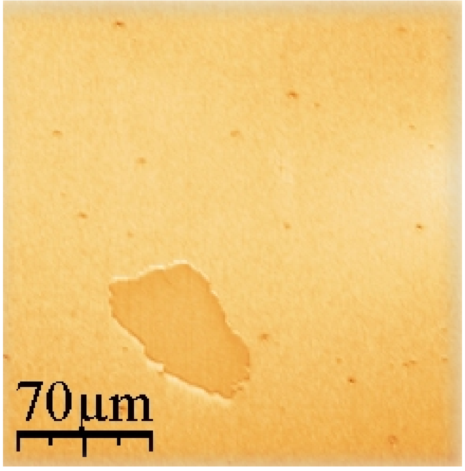


Figure S7. AFM image of surface relief grating spot using a thin film of **3a** on a glass substrate.

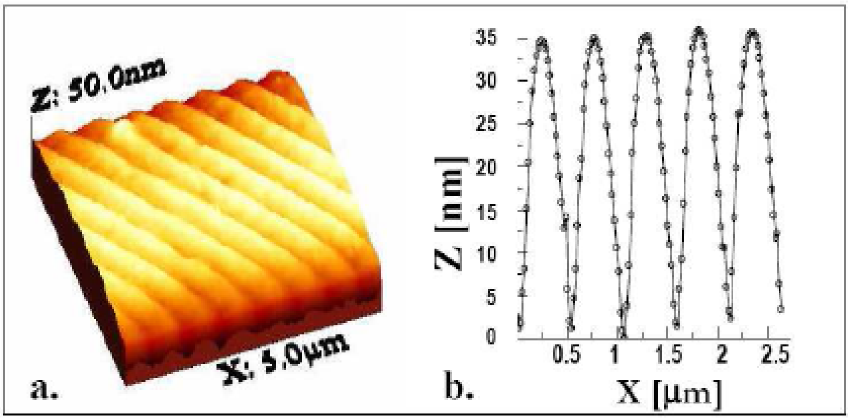


Figure S8. Sinusoidal surface relief grating, inscribed at 10 GW cm^{-2} (in polarization *s-s*) into the amorphous thin film of complex **3a** as measured using atomic force microscopy.

References for Supporting Information

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