Electronic Supplementary Material (ESI) for Polymer Chemistry

Supporting Information:

New Insights in Radical and Cationic Polymerizations upon Visible Light Exposure: Role of Novel Photoinitiator Systems Based on The Pyrene Chromophore.

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Figure 1. UV-visible absorption spectra of **Py** and **A_3** in toluene.

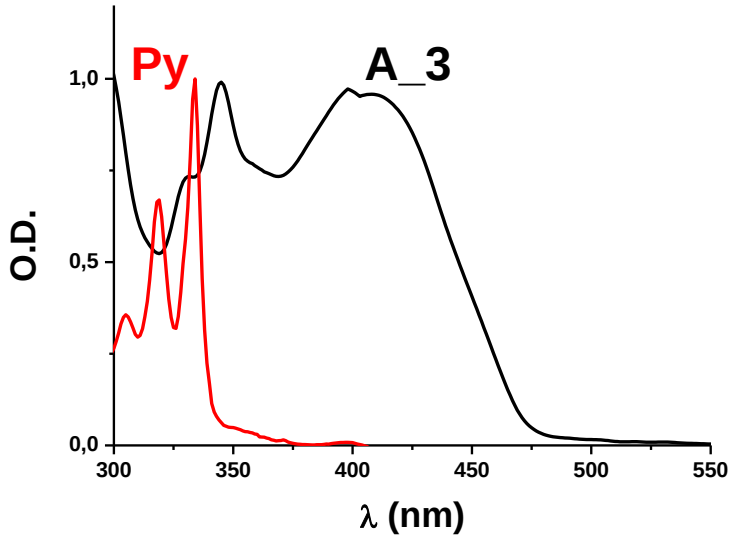


Figure 2. Photopolymerization profiles of **EPOX** under air upon a laser diode at 457 nm exposure in the presence of: (**1**) **A_3**/Iod2 (0.2%/2% w/w); (**2**) **A_3**/$(TMS)_3$Si-H/Iod2 (0.2%/3 %/2% w/w) under air; insert: Si-H conversion during the photopolymerization of (2).

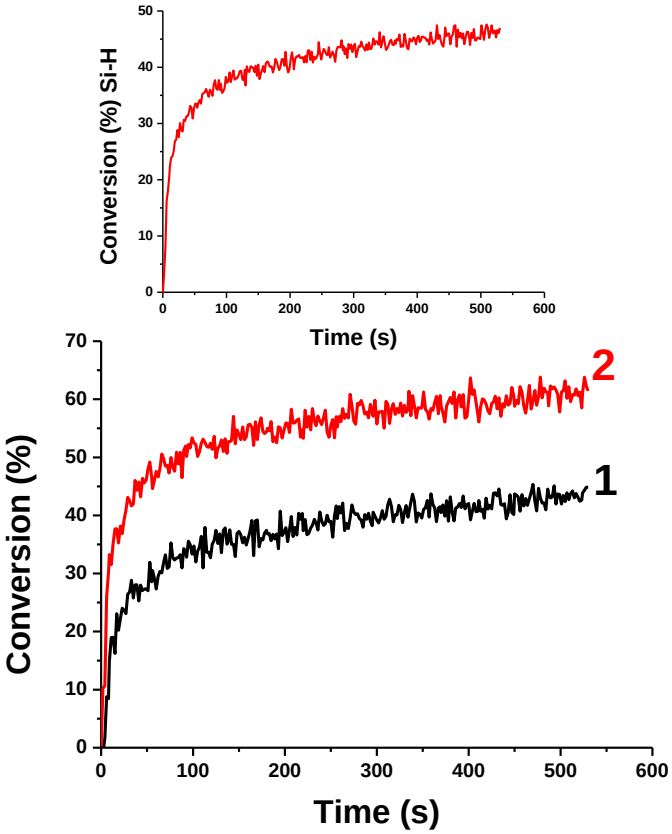


Figure 3. Photopolymerization profiles of TMPTA in laminated conditions upon a laser diode at 457 nm exposure in the presence of: (1) methyldiethanolamine/phenacylbromide (4.5%/3% w/w); (2) **A_3**/methyldiethanolamine/phenacylbromide (0.4%/4.5%/3% w/w).

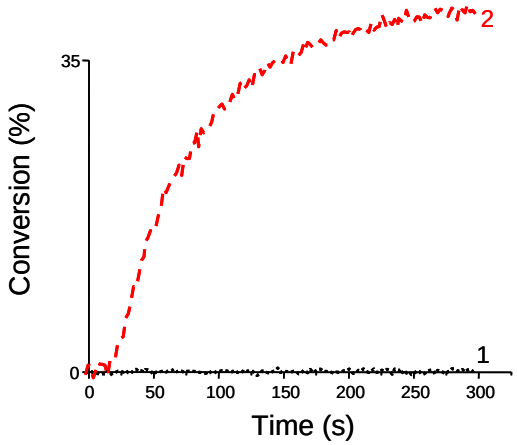
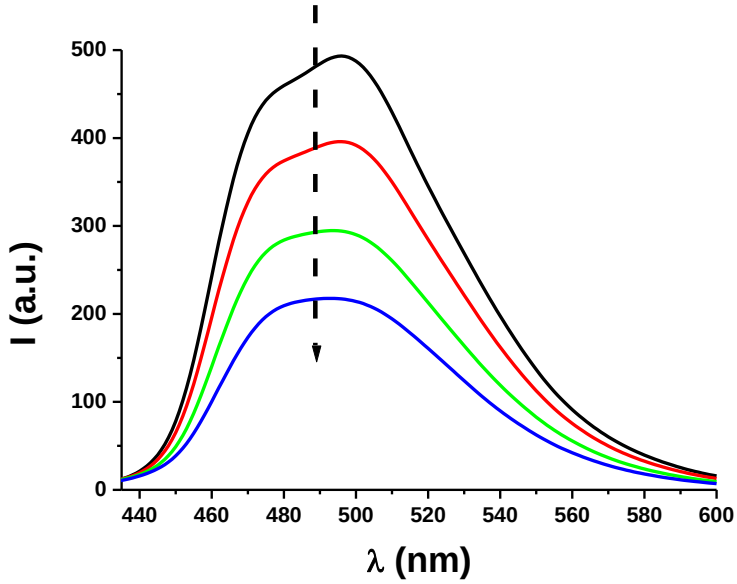
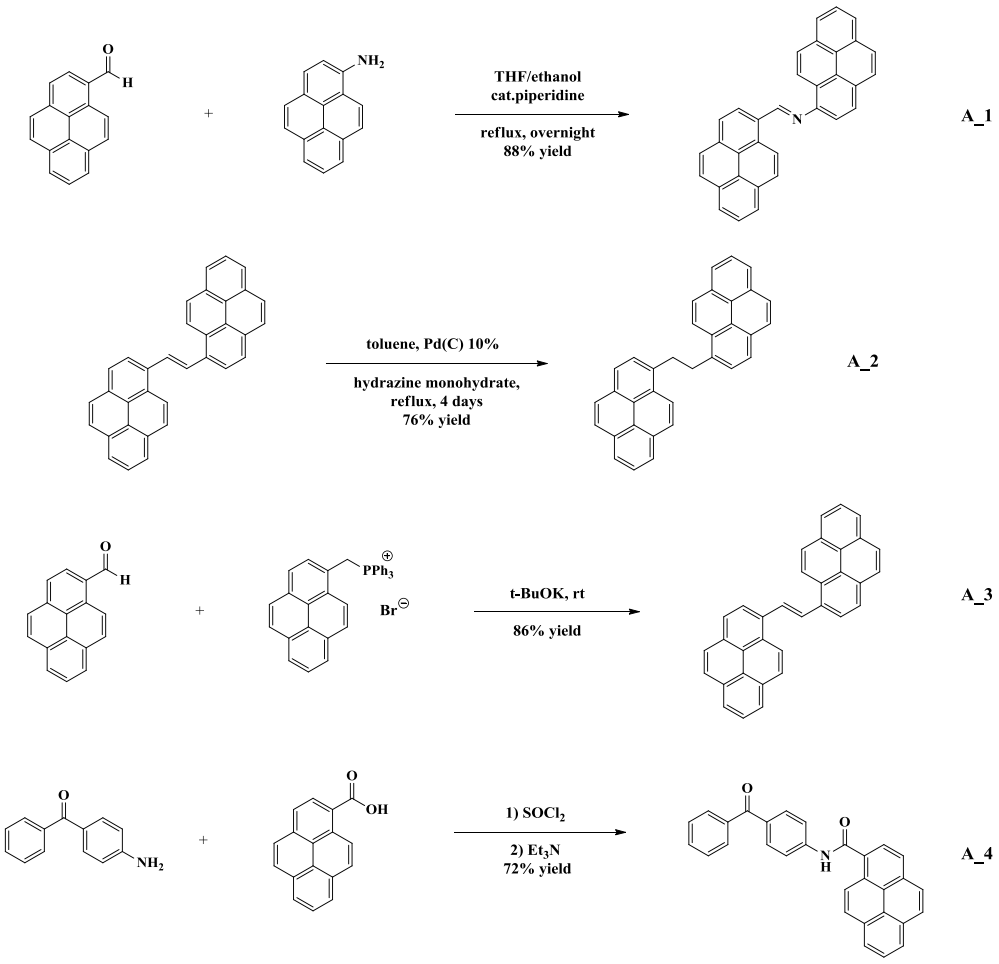
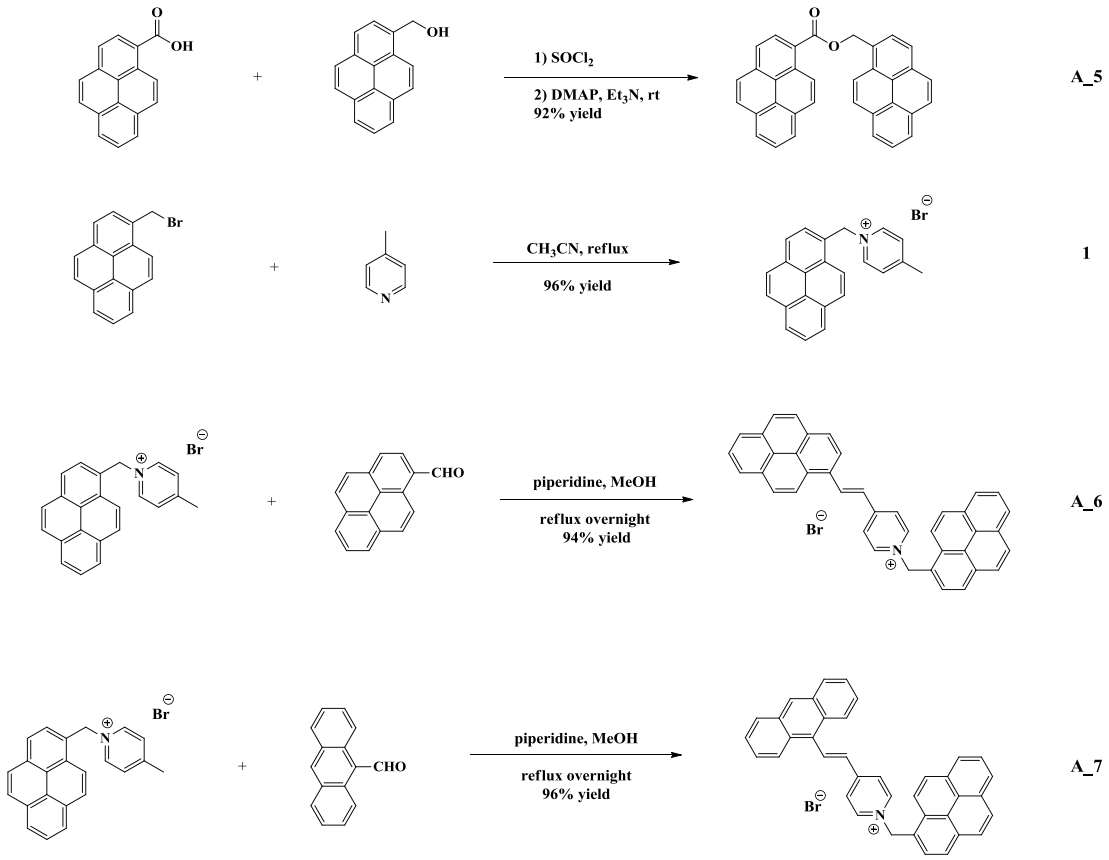


Figure 4. Fluorescence quenching ^{1}**A_2**/Iod2.



Synthesis of the different compounds:

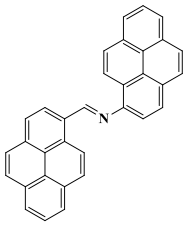




All reagents and solvents were purchased from Aldrich or Alfa Aesar and used as received without further purification. Mass spectroscopy was performed by the Spectropole of Aix-Marseille University. ESI mass spectral analyses were recorded with a 3200 QTRAP (Applied Biosystems SCIEX) mass spectrometer. The HRMS mass spectral analysis was performed with a QStar Elite (Applied Biosystems SCIEX) mass spectrometer. Elemental analyses were recorded with a Thermo Finnigan EA 1112 elemental analysis apparatus driven by the Eager 300 software. ^{1}H and ^{13}C NMR spectra were determined at room temperature in 5 mm o.d. tubes on a Bruker Avance 400 spectrometer of the Spectropole: ^{1}H (400 MHz) and ^{13}C (100 MHz). The ^{1}H chemical shifts were referenced to the solvent peak $CDCl_3$ (7.26 ppm), DMSO-d_6 (2.49 ppm) and the ^{13}C chemical shifts were referenced to the solvent peak $CDCl_3$ (77 ppm), DMSO-d_6 (39.5 ppm). 1-Bromomethylpyrene and triphenyl(pyren-1-ylmethyl)phosphonium bromide were prepared following procedures previously reported in the literature without modification and with similar yields.[1] All reactions were performed under inert atmosphere in the dark.

[1] W. Chen, N. B. Zuckerman, J. W. Lewis, J. P. Konopelski, S. Chen, *J. Phys. Chem. C* **2009,** *113*, 16988–16995.

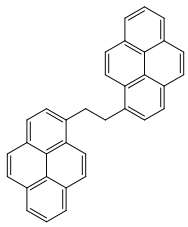
(*E*)-*N*-(Pyren-1-ylmethylene)pyren-1-amine A_1.



A_1

0.5 g (2.17 mmol) of pyrene-1-carbaldehyde and 0.472 g (2.17 mmol) of 1-aminopyrene were suspended in a mixture of 100 mL absolute ethanol and 100 mL THF. 0.5 mL of piperidine was added to the solution and the reaction was refluxed overnight. During the reflux, a brown-red precipitate formed. It was filtered off, washed with pentane and dried under vacuum. The title compound proved to be highly insoluble (820 mg, 88% yield). ^{1}H NMR (DMSO-d_6) δ (ppm): 8.11-8.54 (m, 15H), 8.87 (d, 1H, J = 8.8 Hz), 9.12 (d, 1H, J = 8.1 Hz), 9.50 (d, 1H, J = 9.0 Hz), 10.0 (s, 1H, CH=N); Anal. Calc. for $C_{33}H_{19}N$: C, 92.3; H, 3.2; N, 10.7 Found: C, 92.1; H, 3.3; N, 10.5%; HRMS (ESI MS) *m*/*z*: theor: 430.1590 found: 430.1588 ($[M+H]^+$ detected).

(*E*)-1,2-Di(pyren-1-yl)ethane A_2.

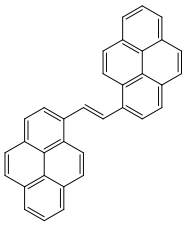


A_2

100 mg (0.233 mmol) of alkene **A_3** were suspended in 200 mL toluene and 40 mg of Pd (10% on charcoal) was added to the solution. 5 mL hydrazine monohydrate was added and the solution was refluxed for four days. After cooling, palladium was removed by filtration on celite and the solution was concentrated to dryness. The residue was purified by column chromatography (SiO_2) using a gradient of solvent ranging from pentane to DCM 1/1. The title compound was isolated as a yellow solid (76 mg, 76% yield). ^{1}H NMR ($CDCl_3$) δ (ppm): 3.06 (s, 4H, CH_2), 7.94 (d, 2H, J = 8.5 Hz), 8.10-8.30 (m, 16H); ^{13}C NMR ($CDCl_3$) δ (ppm):

30.3, 123.5, 124.5, 124.7, 125.5, 125.6, 126.3, 126.9, 127.4, 127.7, 128.2, 129.0, 129.6, 130.9, 131.3, 132.0, 135.7; HRMS (ESI MS) *m*/*z*: theor: 430.1722 found: 430.1726 ($M^{+\cdot}$ detected).

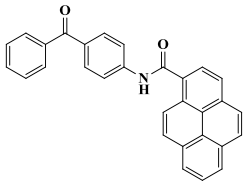
(*E*)-1,2-Di(pyren-1-yl)ethene A_3.



A_3

To a solution of 1-pyrenecarboxaldehyde (0.22 g, 0.94 mmol) and triphenyl(pyren-1-ylmethyl)phosphonium bromide (0.72 g, 1.3 mmol) in 80 mL dry THF was added at room temperature in one portion *t*-BuOK (0.16 g, 1.3 mmol) at room temperature. Immediately after the addition of *t*-BuOK, the reaction became orange and the solution was allowed to stir for 3 hours in the dark. The first precipitate was filtered off. Concentration of the solution to 2/3 of its initial volume and addition of pentane provided a second precipitate which was filtered off, washed with pentane and dried. The solid was purified by column chromatography (SiO_2) using a mixture 1/1 of pentane/DCM as the eluent. After concentration of the solution, the solid was suspended in pentane, filtered off and dried under vacuum (346 mg, 86% yield). ^{1}H NMR ($CDCl_3$) δ (ppm): 8.01-8.05 (m, 3H), 8.11 (d, 3H, J = 2.5 Hz), 8.18 (d, 2H, J = 9.3 Hz), 8.22 (d, 4H, J = 7.5 Hz), 8.28 (d, 2H, J = 8.0 Hz), 8.46 (s, 2H), 8.56 (d, 2H, J = 8.0 Hz), 8.62 (d, 2H, J = 9.3 Hz); ^{13}C NMR ($CDCl_3$) δ (ppm): 123.2, 123.9, 125.0, 125.1, 125.3, 125.4, 126.1, 126.4, 127.4, 127.8, 127.9, 128.6, 129.0, 131.0, 131.1, 131.6, 132.9; HRMS (ESI MS) *m*/*z*: theor: 429.1638 found: 429.2635 ($[M+H]^+$ detected).

***N*-(4-Benzoylphenyl)pyrene-1-carboxamide A_4.**

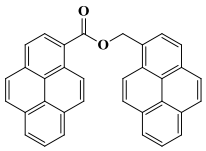


A_4

Pyrene-1-carboxylic acid (0.5 g, 2.03 mmol) was suspended in 10 mL of thionyl chloride and the reaction was refluxed in the dark for 3 hours. After cooling, the solvent was removed under reduced pressure and furnished a light yellow solid. It was dissolved in 10 mL dry

DCM and added to an ice-cooled solution of 4-aminobenzophenone (0.4 g, 2.03 mmol) and 0.27 mL (2 mmol) of triethylamine. The reaction mixture was stirred at room temperature overnight. Water was added and the solution was extracted with ethyl acetate several times. The organic phases were combined, dried over magnesium sulfate and the solvent removed under reduced pressure. The residue was purified by column chromatography (SiO_2) and eluted with DCM and methanol. Caution: the product is hardly removable from the silicagel even with methanol. The solid was purified by precipitation with pentane from a solution of DCM (698 mg, 82% yield). ^{1}H NMR ($CDCl_3$) δ (ppm): 1.62 (brs, NH), 7.49-7.53 (m, 2H), 7.59-7.63 (m, 1H), 7.82 (d, 2H, J = 7.3 Hz), 7.90-7.93 (m, 4H), 8.06-8.29 (m, 8H), 8.62 (d, 1H, J = 9.3 Hz); ^{13}C NMR ($CDCl_3$) δ (ppm): 112.5, 119.2, 120.6, 123.6, 123.7, 123.8, 124.2, 124.4, 125.4, 125.5, 125.8, 126.3, 126.6, 126.7, 127.1, 127.8, 127.9, 128.3, 128.4, 129.0, 130.0, 130.1, 130.7, 131.1, 132.5, 137.5, 143.5, 153.8, 168.1, 194.6; HRMS (ESI MS) *m*/*z*: theor: 426.1489 found: 426.1485 ($[M+H]^+$ detected).

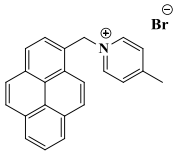
Pyren-1-ylmethyl pyrene-1-carboxylate A_5.



A_5

0.5 g (2.03 mmol) of Pyrene 1-carboxylic acid was suspended in 15 mL $SOCl_2$ and a few drops of DMF. The solution was refluxed for two hours and the solvents were removed under reduced pressure. 20 mL of dry THF were then added. A solution of 0.47 g (2.03 mmol) of 1-aminopyrene, 0.25 g (2.04 mmol) of DMAP and 0.3 mL (1.97 mmol) of triethylamine was separately prepared. The solution of acid chloride was added to the former one at 0°C and stirring was maintained at room temperature overnight. The solution was then refluxed for 2 hours. Chloroform was added and the solution was washed several times with water, dried over magnesium sulfate and the solvent removed under reduced pressure. The residue was purified by column chromatography (SiO_2) using a gradient of eluent (from pentane to DCM and finally acetone) (847mg, 92% yield). ^{1}H NMR ($CDCl_3$) δ (ppm): 5.37 (s, 2H), 7.96-8.15 (m, 18H); Anal. Calc. for $C_{34}H_{20}O_2$: C, 88.7; H, 4.4; O, 6.9; Found: C, 88.2; H, 4.0; O, 6.5%; HRMS (ESI MS) *m*/*z*: theor: 461.1536 found: 461.1532 ($[M+H]^+$ detected).

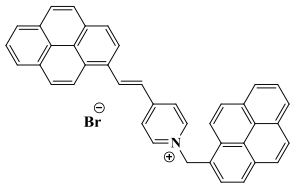
4-Methyl-1-(pyren-1-ylmethyl)pyridin-1-ium bromide 1



1

2.54 g (8.6 mmol) of 1-(Bromomethyl)pyrene and 2 mL of 4-picoline were dissolved in 60 mL acetonitrile and the solution was refluxed overnight. After cooling, the solvent was removed under reduced pressure and a light beige solid formed. The solid was filtered off, washed several times with ether and dried under vacuum (3.20 g, 96% yield). ^{1}H NMR (DMSO-d_6) δ (ppm): 2.34 (s, 3H), 6.63 (s, 1H), 7.29 (d, 2H, J = 5.1 Hz), 7.99 (d, 2H, J = 6.4 Hz), 8.16 (t, 2H, J = 8.2 Hz), 8.25 (d, 1H, J = 9.1 Hz), 8.30 (d, 1H, J = 9.1 Hz), 8.36-8.49 (m, 5H), 9.05 (d, 1H, J = 6.5 Hz); ^{13}C NMR (DMSO-d_6) δ (ppm): 20.5, 64.9, 122.2, 123.6, 124.1, 124.8, 125.3, 126.0, 126.2, 126.6, 126.8, 127.2, 128.4, 128.5, 128.7, 129.1, 130.1, 130.7, 131.8, 143.7, 147.7, 148.6, 159.5; HRMS (ESI MS) *m*/*z*: theor: 308.1434 found: 308.1436 ($M^{+\cdot}$ detected).

(*E*)-4-(2-(3a^1,5a^1-Dihydropyren-1-yl)vinyl)-1-(pyren-1-ylmethyl)pyridin-1-ium bromide A_6.

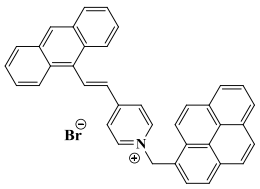


A_6

1.84 g (4.74 mmol) of 4-methyl-1-(pyren-1-ylmethyl)pyridin-1-ium bromide, 1.3 g (5.69 mmol, 1.2 eq.) of pyrene 1-carbaldehyde were suspended in 50 mL methanol and 2 mL of piperidine was added. The reaction mixture was refluxed overnight. After cooling, the precipitate was filtered off, washed with THF, DCM and pentane (2.67 g, 94% yield). ^{1}H NMR (DMSO-d_6) δ (ppm): 6.64 (s, 2H), 7.87 (d, 1H, J = 16 Hz), 8.11-8.19 (m, 6H), 8.24-8.32 (m, 6H), 8.38-8.48 (m, 5H), 8.54-8.57 (m, 2H), 8.66 (d, 1H, J = 8.3 Hz), 8.94 (d, 1H, J = 9.4 Hz), 9.12-9.16 (m, 2H); ^{13}C NMR (DMSO-d_6) δ (ppm): 60.1, 122.3, 123.1, 123.6, 123.7, 124.1, 124.2, 124.3, 124.5, 125.3, 125.4, 125.6, 125.9, 126.0, 126.2, 126.3, 126.7, 126.8,

127.0, 127.2, 127.3, 128.1, 128.4, 128.5, 128.7, 128.8, 128.9, 129.1, 129.3, 129.4, 129.5, 130.1, 130.2, 130.7, 130.8, 131.7, 132.3, 137.3, 144.2, 153.3; HRMS (ESI MS) *m*/*z*: theor: 520.2060 found: 520.2051 ($M^{+\cdot}$ detected).

(*E*)-4-(2-(Anthracen-9-yl)vinyl)-1-(pyren-1-ylmethyl)pyridin-1-ium bromide A_7.



A_7

2.33 g (6 mmol) of 4-Methyl-1-(pyren-1-ylmethyl)pyridin-1-ium bromide, 1.86 g (9 mmol, 1.5 eq.) of anthracene 9-carbaldehyde were suspended in 50 mL methanol and 2 mL of piperidine was added. The reaction mixture was refluxed overnight. After cooling, the precipitate was filtered off, washed with THF, DCM and pentane (3.32 g, 96% yield). ^{1}H NMR (DMSO-d_6) δ (ppm): 6.68 (s, 2H), 7.35 (d, 1H, J = 16.5 Hz), 7.56-7.62 (m, 5H), 8.15-8.20 (m, 5H), 8.31 (d, 2H, J = 6.7 Hz), 8.35-8.38 (m, 2H), 8.44-8.50 (m, 3H), 8.51-8.58 (m, 3H), 8.71 (s, 1H), 8.96 (d, 1H, J = 16.5 Hz), 9.22 (d, 1H, J = 6.8 Hz); Anal. Calc. for $C_{38}H_{26}BrN$: C, 79.2; H, 4.5; N, 2.4; Found: C, 78.9; H, 4.4; N, 2.5%; HRMS (ESI MS) *m*/*z*: theor: 496.2060 found: 496.2059 ($M^{+\cdot}$ detected).