

Exploration of photodegradation mechanism of naphtho[2,3-*g*]quinoxalines and pyrazino[2,3-*b*]phenazines

Supporting Information

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Experimental Details

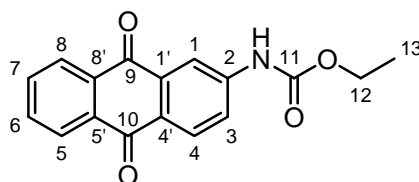
The used reagents and solvents were purchased from commercial suppliers and were used without further purification. Dry THF was prepared by distillation from sodium/benzophenone under nitrogen atmosphere. The silica gel used for column chromatography possessed a particle size of 40-63 μm . 4,4'-bis(trifluoromethyl)benzyl was synthesized according to the literature procedure¹.

¹H- and ¹³C-NMR spectra were recorded on a 300 (Avance-II, Avance-III), 500 (DRX500) or 600 (Avance-III) MHz spectrometer manufactured by Bruker Biospin, Karlsruhe.

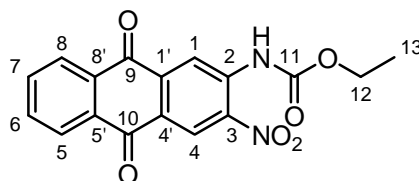
Measurements at 500.15 MHz ¹H frequency were performed on a Bruker DRX 500 spectrometer equipped with a 5 mm triple-band inverse probe (1H, 2H, 31P, BB) with z-gradient. The spectra were measured without sample rotation at 300 K, temperature control was achieved with a BCU-X.

Measurements at 600.4 MHz ¹H frequency were performed on a Bruker Avance III 600 spectrometer equipped with a 5 mm triple-band inverse probe (1H, 2H, 31P, BB) with z-gradient. The spectra were measured without sample rotation at 300 K, temperature control was achieved with a BCU-Xtreme.

Chemical shifts (δ) are listed in parts per million (ppm). The values are reported relative to the solvent residual peaks of CDCl₃, CD₂Cl₂, and THF-d₈ present in the deuterated solvents². The chemical shifts of the degradation intermediated and products from **7a** and **9a** are reported versus TMS (0 ppm) as internal standard. MS spectra were recorded on a Finnigan MAT 95 spectrometer and EI ionization was used.

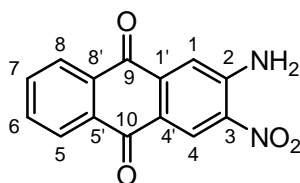


Anthraquinone-2-urethane (2)³ 17.82 g (80 mmol, 1.0 eq) of 2-aminoanthracene are dissolved in 170 mL nitrobenzene. Afterwards 13.2 mL (111 mmol, 1.7 eq) ethylchloroformiate are added and the mixture is heated at 160°C for 45 minutes. The reaction mixture is then cooled down to room temperature and the precipitate is filtered off and washed with acetone. The solid is then dried in vacuum. 20.16g (69 mmol, 86%) anthrachinone-2-urethane could be isolated. EI-MS: m/z = 295 found.

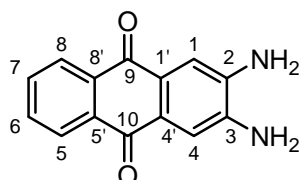


3-nitroanthraquinone-2-urethane (3)³ 10 g (34 mmol, 1.0 Äq) anthraquinone-2-urethane are dissolved in 50 mL sulfuric acid (98%). The red solution is cooled to 0°C. Meanwhile 2.5 mL concentrated nitric acid and 25 mL sulfuric acid (98°C) are mixed and the resulting solution is added drop wise to the anthraquinone-2-urethane solution. Afterwards the mixture

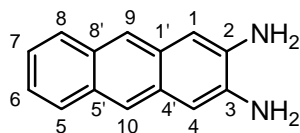
is stirred at 0°C for 2 hours. Subsequently the mixture is poured in 600 mL icewater. The precipitate is filtered off and dried under reduced pressure. The raw product is recrystallized from nitrobenzene giving 5.68 g (17 mmol, 49%) of 3-nitroanthraquinone-2-urethane. ¹H-NMR (500 MHz, C₆D₆, 300 K): δ = 0,937 (t, CH₃, 13-H₃), 3,925 (q, CH₂, 12-H₂) 7,054 (m, CH, 5/8-H₂), 8,120-8,182 (m, CH, 6/7-H₂), 8,911 (s, 4-H), 9,608 (s, CH, 1-H), 9,764 (s, NH, H₁) ppm. ¹³C-NMR (125 MHz, CDCl₃, 300 K): δ = 14,77 (13-C), 63,00 (12-C), 119,92 (1-C), 126,76 (4-C), 127,61 (3-C), 127,90/128,11 (6/7-C), 134,35/134,44 (5'/8'-C), 134,66/134,92 (5/8-C), 138,21 (2-C), 138,73 (4'-C), 139,92 (1'-C), 152,97 (11-C), 180,53 (10-C), 181,67 (9-C) ppm.



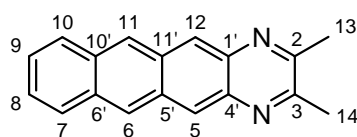
2-amino-3-nitroanthraquinone (4)³ 4.498 g (13 mmol, 1.0 eq) 3-nitroanthraquinone-2-urethane are dissolved in 4 mL water and 23 mL concentrated sulfuric acid. The red solution is heated at 110°C for one hour and then cooled to room temperature. Then the mixture is poured in 100 mL of ice cooled water and the built yellow precipitate is filtered off and dried under reduced pressure. The product was used without further purification in the next synthesis.



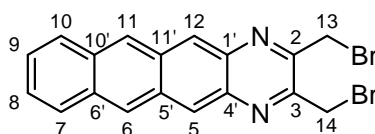
2,3-diaminoanthraquinone (5)³ The 2-amino-3-nitroanthraquinone from the above described step was suspended in 25 mL water. Afterwards 10.65 g Na₂S * 9 H₂O (44 mmol, 4.4 eq) are added in portions to the suspensions. After addition of the whole Na₂S * 9 H₂O the mixture is heated at 90°C for 1 hour. The mixture is cooled to room temperature and the red precipitate is filtered off. The red residue is washed with water and then dried under reduced pressure giving 2.39 g (0,01 mol, 77% over the two reaction steps) 2,3-diaminoanthraquinone as red solid. ¹H-NMR (500 MHz, THF-d₈, 300 K): 5,128 (NH₂, H₄), 7,417 (s, CH, 1/4-H₂), 7,722 (m, CH, 6/7-H₂), 8,187 (m, CH, 5/8-H₂) ppm. ¹³C-NMR (125 MHz, THF-d₈, 300 K): 112,81 (1/4-C), 127,80 (5/8-C) 127,91 (1'/4'-C), 134,28 (6/7-C), 136,17 (5'/8'-C), 142,36 (2/3-C), 183,19 (9/10-C) ppm.



2,3-diaminoanthracene (6) Zinc powder (57,3 g) is stirred with a solution of 0,1 g copper sulfate pentahydrate in 3,5 mL water for 15 minutes. Afterwards 20.39 g (86 mmol, 1 eq) 2,3-diaminoanthraquinone and 285 mL aqueous NaOH (5%) are added. The mixture is heated at 140°C until the color changes to yellow. Then the mixture is heated for 19 hours at 160°C. The mixture is filtered hot and the residue is dried. Subsequently the residue is extracted with THF, the filtrate and then the solvent is evaporated. The raw product is then crystallized from nitrobenzene giving 4.00 g (19 mmol, 22%) of 2,3-diaminoanthracene. Purity was further increased by crystallization from hot toluene giving 2,3-diaminoanthracene as gold leaflets. ¹H-NMR (500 MHz, THF-d₈, 300 K): 4,608 (NH₂, H₄), 7,047 (s, CH, 1/4-H₂), 7,224 (m, CH, 6/7-H₂), 7,802 (m, CH, 5/8-H₂), 7,963 (s, CH, 9/10-H₂) ppm. ¹³C-NMR (125 MHz, THF-d₈, 300 K): 108,24 (1/4-C), 123,15 (9/10-C), 124,47 (6/7-C), 129,02 (6/8-C), 131,58 (1'/4'-C), 131,91 (5'/8'-C), 140,63 (2/3-C) ppm. EI-MS: m/z = 208 found.



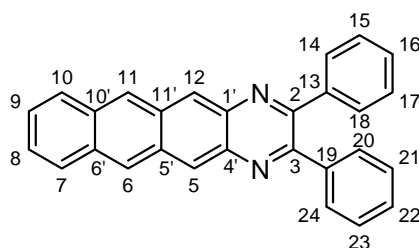
2,3-dimethylnaptho[2,3-g]quinoxaline (7a) 2.508 g (12 mmol, 1 eq) 2,3-diaminoanthracene are suspended in 90 mL dry THF and then heated to 65°C. Then 10.75 mL (123 mmol, 10 eq) 2,3-butanedione are added. The mixture is stirred for 20 minutes and then is cooled down in the dark. The precipitate is filtered off and the recrystallized from toluene giving 2.163 g (8 mmol, 69%) of 2,3-dimethylnaptho[2,3-g]quinoxaline as orange crystals. ¹H-NMR (600 MHz, THF-d₈, 300 K): 2.61 (s, CH₃, 13/14-H₆), 7.31 (dd, CH_{arom}, 8/9-H₂), 7.92 (dd, CH_{arom}, 7/10-H₂), 8.60 (s, CH_{arom}, 6/11-H₂), 8.66 (s, CH_{arom}, 5/12-H₂) ppm. ¹³C-NMR (150 MHz, THF-d₈, 300 K): 22.4 (13/14-C), 125.0 (8/9-C), 126.1 (6/11-C), 126.2 (5/12-C), 127.7 (7/10-C), 131.0 (5'/11'-C), 131.6 (6'/10'-C), 137.7 (1'/4'-C), 154.5 (2/3-C) ppm. EI-MS: m/z = 258 found.



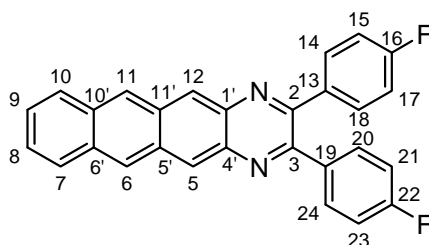
2,3-bis(bromomethyl)naptho[2,3-g]quinoxaline (7b) 0.690 g (3.3 mmol, 1 eq) 2,3-diaminoanthracene are suspended in 50 mL dry THF and then 0.809 g (3.3 mmol, 1 eq) 1,4-dibromo-2,3-butanedione are added. The mixture is heated to 70°C for 20 minutes and then is cooled down in the dark. The precipitate is filtered off and washed with THF. 1.232 g (2.9 mmol, 90%) of 2,3-bis(bromomethyl)naptho[2,3-g]quinoxaline as purple crystals could be isolated. ¹H-NMR (500 MHz, THF-d₈, 300 K): 5,077 (s, CH₂, 13/14-H₄), 1,7547 (m, CH_{arom}, 8/9-H₂), 8,150 (m, CH_{arom}, 7/10-H₂), 8,943 (s, CH_{arom}, 6/11-H₂), 8,960 (s, CH_{arom}, 5/12-H₂) ppm. ¹³C-NMR (125 MHz, THF-d₈, 300 K): 32,85 (13/14-C), 127,96 (8/9-C), 129,00 and 129,82 (6/11/5/12-C), 130,01 (7/10-C), 133,87 (5'/11'-C), 134,50 (6'/10'-C), 139,09 (1'/4'-C), 153,21 (2/3-C) ppm. EI-MS: m/z = 416 found.

General procedure for naphtho[2,3-*g*]quinoxalines (7c-f) In a 100-mL-round bottomed flask 1 equivalent of 2,3-diaminoanthracene is suspended in dry THF (25 mL per 0,5 g 2,3-diaminoanthracene). Afterwards 1 equivalent of the appropriate diketone and 1 mL acetic acid is added to the reaction mixture. The mixture is stirred at the given time for the given temperature (see table1) and the cooled down to room temperature in the dark. Then the mixture is filtrated and the solvent is evaporated. The received residue is extracted with n-Hexane and crystallized from toluene. The yields are given in table 1.

R	temperature [°C]	time [min]	yield [%]
c) C ₆ H ₅	70	30	88
d) C ₆ H ₄ F	70	20	36
e) C ₆ H ₄ Br	60	20	96
f) C ₆ H ₄ OCH ₃	76	50	77

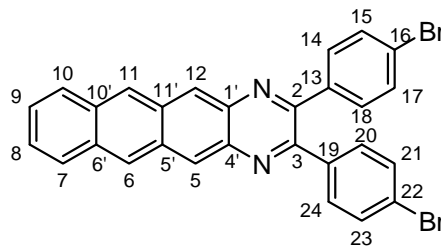


2,3-diphenylnaphtho[2,3-*g*]quinoxaline (7c) ¹H-NMR (500 MHz, CD₂Cl₂, 300 K): 7,385 (m, CH_{arom} 15/17/21/23-H₄), 7,431 (m, CH_{arom}, 16/22-H₂), 7,467 (m, CH_{arom}, 8/9-H₂), 7,591 (m, CH_{arom}, 14/18/20/24-H₄), 8,031 (m, CH_{arom}, 7/10-H₂), 8,748 (s, CH_{arom}, 6/11-H₂), 8,899 (s, CH_{arom}, 5/12-H₂) ppm. ¹³C-NMR (125 MHz, CD₂Cl₂, 300 K): 126,77 (8/9-C), 127,75 (6/11-C), 128,46 (5/12-C), 128,85 (15/17/21/23-C), 129,00 (7/10-C), 129,802 (16/22-C), 130,64 (14/18/20/24-C) 132,67 (5'-11'-C), 132,99 (6'/10'-C), 138,14 (1'/4'-C), 140,13 (13/19-C), 155,06 (2/3-C) ppm. EI-MS: m/z = 382 found.

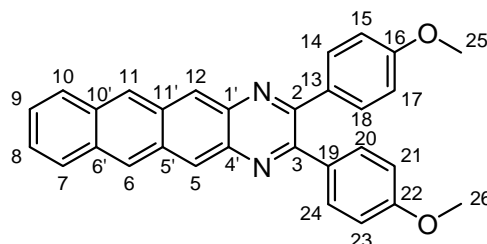


2,3-bis(4-fluorophenyl)naphtho[2,3-*g*]quinoxaline (7d) ¹H-NMR (500 MHz, CDCl₃, 300 K): 7,091 (t, CH_{arom}, 15/17/21/23-H₄), 7,480 (m, CH_{arom}, 8/9-CH₂), 7,579 (m, CH_{arom}, 14/18/20/24-H₄), 8,045 (m, CH_{arom}, 7/10-H₂), 8,776 (s, CH_{arom}, 6/11-H₂), 8,968 (s, CH_{arom}, H₂) ppm. ¹³C-NMR (125 MHz, CDCl₃, 300 K): 115,87 (d, ²J_(C,F) 21,35 Hz, 15/17/21/23-C), 126,51 (8/9-C), 127,49 (6/11-C), 128,19 (5/12-C), 128,64 (7/10-C), 132,15 (d, ³J_(C,F) 8,54 Hz,

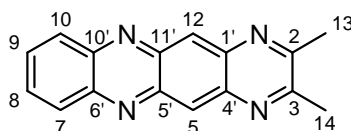
14/18/20/24-C), 132,34 (5'/11'-C), 132,74 (6'/10'-C), 135,32 (13/19-C), 137,42 (1'/4'-C), 153,31 (2/3-C), 162,81 und 164,80 (d, $^1J_{(C,F)}$ 250,45 Hz, 16/22-C) ppm. EI-MS: m/z = 418 found.



2,3-bis(4-bromophenyl)naphtho[2,3-g]quinoxaline (7e) $^1\text{H-NMR}$ (500 MHz, THF-d_8 , 300 K): 7,527 (m, CH_{arom} , 8/9- H_2), 7,619 (m, CH_{arom} , 14/15/17/18/20/21/23/24- H_8), 8,132 (m, CH_{arom} , 7/10- H_2), 8,916 (s, CH_{arom} , 4/11- H_2), 9,008 (s, CH_{arom} , 5/12- H_2) ppm. $^{13}\text{C-NMR}$ (125 MHz, THF-d_8 , 300 K): 125,25 (16/22-C), 127,75 (8/9-C), 128,82 (6/11-C), 129,57 (5/12-C), 129,99 (7/10-C), 133,03 und 133,50 (14/15/17/18/20/21/23/24-C), 133,93 (5'/11'-C), 134,34 (6'/10'-C), 139,15 (4'/1'-C), 140,23 (13/19-C), 154,48 (2/3-C) ppm.



2,3-bis(4-methoxyphenyl)naphtho[2,3-g]quinoxaline (7f) $^1\text{H-NMR}$ (500 MHz, THF-d_8 , 300 K): 3,879 (s, CH_3 , 25/26- H_6), 6,969 (d, CH_{arom} , 15/17/21/23- H_2), 7,485 (m, CH_{arom} , 8/9- H_2), 7,662 (d, CH_{arom} , 14/18/20/24- H_4), 8,099 (m, CH_{arom} , 7/10- H_2), 8,844 (s, CH_{arom} , 6/11- H_2), 8,912 (s, CH_{arom} , 5/12- H_2) ppm. $^{13}\text{C-NMR}$ (125 MHz, THF-d_8 , 300 K): 56,35 (25/26-C), 115,01 (15/17/21/23-C), 127,37 (8/9-C), 128,52 (6/11-C), 128,86 (5/12-C), 129,94 (7/10-C), 133,12 (14/18/20/24-C), 133,75 (5'/11'-C), 133,89 (13/19-C), 134,05 (6'/10'-C), 139,38 (1'/4'-C), 155,49 (2/3-C), 162,55 (16/22-C) ppm. EI-MS: m/z = 442 found.

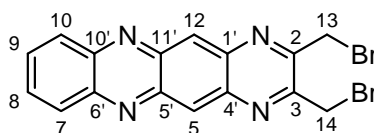


2,3-dimethylpyrazino[2,3-b]phenazine (9a) In a 100-mL round bottomed flask 0.81 g (3.8 mmol, 1 eq) 2,3-diaminophenazine are suspended in 50 mL THF and 2 mL acetic acid are added. Then 3.5 mL (40 mmol, 10 eq) 2,3-butanedione are added and the reaction mixture is stirred for 2 hours at 70°C. The mixture is cooled to room temperature and filtered. The resulting yellow residue is washed with methanol and THF and then dried resulting in 0.615 g (2.4 mmol, 62%) of 2,3-dimethylpyrazino[2,3-b]phenazine. $^1\text{H-NMR}$ (600 MHz, CDCl_3 , 300 K): 2.77 (s, CH_3 , 13/14- H_6), 7.78 (dd, CH_{arom} , 8/9- H_2), 8.20 (dd, CH_{arom} , 7/10- H_2), 8.94 (s,

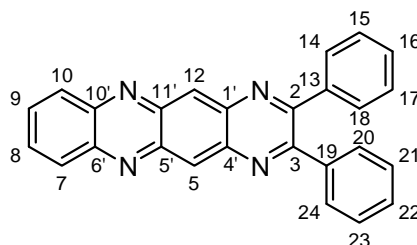
CH_{arom}, 5/12-H₂) ppm. ¹³C-NMR (150 MHz, CDCl₃, 300 K): 23.9 (13/14-C), 128.0 (5/12-C), 129.9 (7/10-C), 131.3 (8/9-C), 140.0 (1'/4'-C), 141.8 (11'/5'-C), 143.7 (6'/10'-C), 155.4 (2/3-C), ppm. EI-MS: m/z = 260 found.

General procedure for pyrazino[2,3-*b*]phenazines (9b-e) In a 100-mL round bottomed flask 1 equivalent of 2,3-diaminophenazine is suspended in methanol (55 mL methanol per 0,5 g 2,3-diaminophenazine) and 1 equivalent of the appropriate diketone and 2 ml acetic acid are added. The reaction mixture is stirred at 70°C for the in table 2 given time. The precipitate is filtered off and the residue is washed with methanol and THF. The achieved yields are listed in table 2.

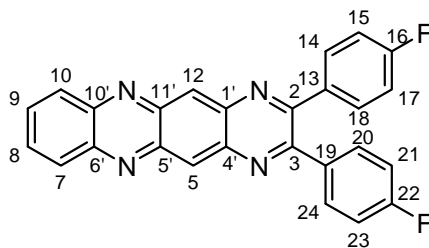
R	temperature [°C]	time [min]	yield [%]
b) CH ₂ Br	70	45	18
c) C ₆ H ₅	70	360	65
d) C ₆ H ₄ F	70	47	72
e) C ₆ H ₄ CF ₃	70	30	53



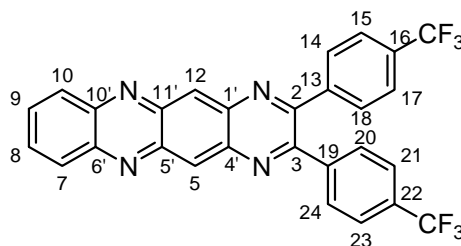
2,3-Bis(bromomethyl)pyrazino[2,3-*b*]phenazine (9b) ¹H-NMR (500 MHz, THF-*d*₈, 300 K): 4,961 (s, CH₂, 13/14-H₄), 7,825 (m, CH_{arom}, 8/9-H₂), 8,158 (m, CH_{arom}, 7/10-H₂), 8,953 (s, CH_{arom}, 5/12-H₂) ppm. EI-MS: m/z = 418 found.



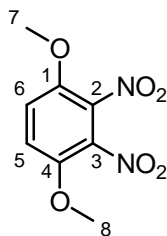
2,3-Diphenylpyrazino[2,3-*b*]phenazine (9c) ¹H-NMR (500 MHz, CDCl₃, 300 K): 7,394 (t, CH_{arom}, 15/17/21/23-H₄), 7,445 (t, CH_{arom}, 16/22-H₂), 7,638 (d, CH_{arom}, 14/18/20/24-H₄), 7,863 (m, CH_{arom}, 8/9-H₂), 8,281 (m, CH_{arom}, 7/10-H₂), 9,214 (s, CH_{arom}, 5/12-H₂) ppm. ¹³C-NMR (125 MHz, CDCl₃, 300 K): 128,69 (15/17/21/23-C), 129,53 (5/12-C), 130,03 (16/22-C), 130,29 (14/18/20/24-C), 130,39 (7/10-C), 131,85 (8/9-C), 138,99 (13/19-C), 140,48/142,52 (1'/4'/5'/11'-C), 145,49 (6'/10'-C), 156,27 (2/3-C) ppm. EI-MS: m/z = 384 found.



2,3-Bis(4-fluorophenyl)pyrazino[2,3-*b*]phenazin (9d) $^1\text{H-NMR}$ (500 MHz, CDCl_3 , 300 K): 7,115 (m, CH_{arom} , 15/17/21/23- H_4), 7,637 (m, CH_{arom} , 14/18/20/24- H_4), 7,874 (m, CH_{arom} , 8/9- H_2), 8,285 (m, CH_{arom} , 7/10- H_2), 9,196 (s, CH_{arom} , 5/12- H_2) ppm. $^{13}\text{C-NMR}$ (125 MHz, CDCl_3 , 300 K): 116,04 (d, $^2J_{\text{C,F}}$ 21,54 Hz, 15/17/21/23-C), 129,52 (5/12-C), 130,35 (7/10-C), 132,05 (8/9-C), 132,38 (d, $^3J_{\text{C,F}}$ 8,45 Hz, 14/18/20/24-C), 134,92 (d, $^4J_{\text{C,F}}$ 3,73 Hz, 13/19-C), 140,32 und 142,52 ($1'/4'/5'/11'$ -C), 145,60 ($6'10'$ -C), 154,89 (2/3-C), 163,16 und 165,14 (d, $^1J_{\text{C,F}}$ 251,04 Hz, 16/22-C) ppm.

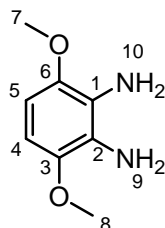


2,3-Bis(4-(trifluoromethyl)phenyl)pyrazino[2,3-*b*]phenazin (9e) $^1\text{H-NMR}$ (500 MHz, CDCl_3 , 300 K): 7,699 (d, CH_{arom} , 15/17/21/23- H_4), 7,770 (d, CH_{arom} , 14/18/20/24- H_4), 7,905 (m, CH_{arom} , 8/9- H_2), 8,300 (m, CH_{arom} , 7/10- H_2), 9,272 (s, CH_{arom} , 5/12- H_2) ppm. $^{13}\text{C-NMR}$ (125 MHz, CDCl_3 , 300 K): 123,18 (CF_3 -C), 125,93 (15/17/21/23-C), 130,10 (5/12-C), 130,38 (7/10-C), 130,66 (14/18/20/24-C), 132,32 (16/22-C), 132,39 (8/9-C), 140,11 ($5'11'$ -C), 141,93 (13/19-C), 142,58 ($1'/4'$ -C), 145,76 ($6'10'$ -C), 154,22 (2/3-C) ppm.



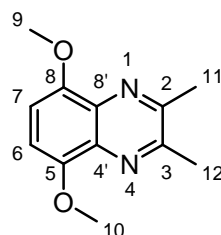
1,4-Dimethoxy-2,3-dinitrobenzene and 1,4-Dimethoxy-2,5-dinitrobenzene (11a/11b)⁴ 13.80 g (100 mmol) 1,4-dimethoxybenzene are dissolved in 23 mL acetic acid and 18 mL concentrated nitric acid are added slowly to the solution. Afterwards another 18 mL are added drop wise. Then the reaction mixture is heated at 80-90°C for five minutes. The reaction is cooled to room temperature and 300 mL water are added. The yellow precipitate is filtered off and dried under reduced pressure giving 19.20 g (84 mmol, 84%) of 11a and 11b. $^1\text{H-NMR}$ (300 MHz, CDCl_3 , 300 K): δ = 3,922 (s, CH_3 , 7/8- H_6), 7,205 (s, CH, 5/6- H_2) ppm. $^{13}\text{C-NMR}$

(75 MHz, CDCl₃, 300 K): δ = 57,85 (7/8-C), 111,55 (2/3-C), 117,05 (5/6-C), 145,65 (1/4-C) ppm.

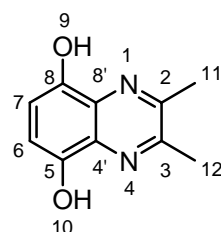


1,2-diamino-3,6-dimethoxybenzene and 1,4-diamino-3,6-dimethoxybenzene (12a/12b)⁵

10.00 g (44 mmol, 1.0 eq) of 1,4-dimethoxy-2,3(2,5)-dinitrobenzol (**12**) are dissolved in 200 mL ethylacetate and 200 mg Pd/C (10%) are added. The mixture is stirred for 24 hours at 50°C at 5 bar hydrogen pressure in a parr autoclave. The catalyst is filtered off via silica gel and the solvent of the filtrate is distilled off. By doing this 5.84 g (35 mmol, 79%) of the white crystalline product are received. ¹H-NMR (300 MHz, CDCl₃, 300 K): δ = 3,499 (s, NH₂, 9/10-H₄), 3,808 (s, CH₃, 7/8-H₆), 6,314 (s, CH, 5/6-H₂) ppm. ¹³C-NMR (75 MHz, CDCl₃, 300 K): δ = 56,29 (7/8-C), 101,02 (4/5-C), 124,91 (1/2-C), 143,50 (3/6-C) ppm.

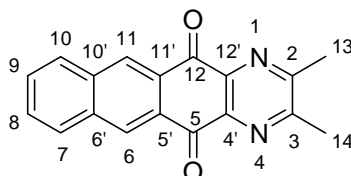


2,3-dimethyl-5,8-dimethoxyquinoxalin (13)⁶ 5.84 g (35 mmol, 1.0 eq) of 12a/12b were dissolved in 150 mL acetic acid and then diluted with 150 mL water. Subsequently 6 mL (68 mmol, 1.9 eq) 2,3-Butandion are added. The reaction mixture is stirred for five minutes at room temperature and then is poured into 500 mL ice water. The yellow precipitate is filtered off and then dried under reduced pressure. By doing so 6.73 g (31 mmol, 89%) 2,3-dimethyl-5,8-dimethoxyquinoxaline could be isolated. ¹H-NMR (300 MHz, CDCl₃, 300 K): δ = 2,760 (s, CH₃, 11/12-H₆), 3,995 (s, CH₃, 9/10-H₆), 6,900 (s, CH, 6/7-H₂) ppm. ¹³C-NMR (75 MHz, CDCl₃, 300 K): δ = 23,52 (11/12-C), 56,48 (9/10-C), 106,78 (6/7-C), 133,83 (4'/8'-C), 148,65 (5/8-C), 153,04 (2/3-C) ppm.

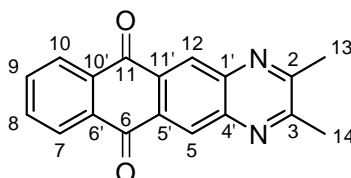


2,3-dimethyl-5,8-dihydroxyquinoxalin (21)⁶ in a dry 500-mL-tree-necked flask 6.42 g (29 mmol, 1.0 eq) 2,3-dimethyl-5,8-dimethoxyquinoxalin and 49 g AlCl₃ are degassed. Under

argon atmosphere 250 mL dry toluene are added. The brown solution is stirred at 110°C for 9 hours. After that the mixture is poured into 500 mL of ice water. The yellow precipitate is filtered off, washed with water and dried under reduced pressure. Afterwards the raw material is recrystallized from ethylacetate giving 4.06 g (21 mmol, 73 %) of 2,3-dimethyl-5,8-dihydroxyquinoxalin. ¹H-NMR (300 MHz, CD₂Cl₂, 300 K): δ = 2,733 (s, CH₃, 11/12-H₆), 7,007 (s, CH, 6/7-H₂), 7,129 (s, OH, 9/10-H₂) ppm. ¹³C-NMR (75 MHz, CD₂Cl₂, 300 K): δ = 23,52 (11/12-C), 110,67 (6/7-C), 131,54 (4'/8'-C), 144,83 (5/8-C), 153,33 (2/3-C) ppm.



2,3-dimethylnaphtho[2,3-g]quinoxaline-5,12-dione (15a) In a dried 100-mL-tree-necked flask 0.56 g (29 mmol, 1.0 eq) 2,3-dimethyl-5,8-dihydroxyquinoxaline and 0.39 g (29 mmol, 1.0 eq) *o*-phthaldialdehyde are dissolved in 13 mL dry and degassed Trifluorethanol under argon atmosphere. Then 0.59 g (55 mmol, 1,9 Äq) Na₂CO₃ are added and the yellow reaction mixture is stirred at 57°C for 90 minutes. After cooling to room temperature 14 mL water are added. The yellow precipitate is filtered off, washed with water and then dried under reduced pressure giving 0.59 g (2 mmol, 70%) of 15a. ¹H-NMR (500 MHz, THF-d₈, 300 K): δ = 2,65 (s, CH₃, 13/14-H₆), 7,62 (dd, CH_{arom.}, 8/9-H₂), 8,10 (dd, CH_{arom.}, 7/10-H₂), 8,78 (s, CH_{arom.}, 6/11-C₂) ppm. ¹³C-NMR (125 MHz, THF-d₈, 300 K): δ = 21,4 (13/14-C), 128,5 (6/11-C), 129,0 (8/9-C), 129,6 (7/10-C), 134,9 (6'/10'-C), 157,5 (2/3-C), 180,1 (5/12-C) ppm.



2,3-dimethylnaphtho[2,3-g]quinoxaline-6,11-dione (15b) 0.362 g (1.5 mmol, 1 eq) 2,3-diaminoathraquinone are dissolved in 40 mL THF and 1.3 mL (15 mmol, 1 eq) 2,3-butanedione and 0.5 mL acetic acid are added. The mixture is stirred for 50 minutes at 70°C. The mixture is then cooled down to room temperature and the solvent and the 2,3-butanedione are evaporated. 0.347 g (1.2 mmol, 80%) 2,3-dimethylnaphtho[2,3-g]quinoxaline-6,11-dione could be isolated. ¹H-NMR (600 MHz, THF-d₈, 300 K): δ = 2.66 (s, CH₃, 13/14-H₆), 7.77 (dd, CH_{arom.}, 8/9-H₂), 8.24 (dd, CH_{arom.}, 7/10-H₂), 8.69 (s, CH_{arom.}, 5/15-H₂) ppm. ¹³C-NMR (150 MHz, THF-d₈, 300 K): δ = 22.2 (13/14-C), 126.6 (7/10-C), 128.3 (5/12-C), 132.1 (5'/11'-C), 133.6 (8/9-C), 134.0 (6'/10'-C), 142.8 (1'/4'-C), 157.2 (2/3-C), 181.1 (6/11-C) ppm.

Determination of HOMO- and LUMO-energies

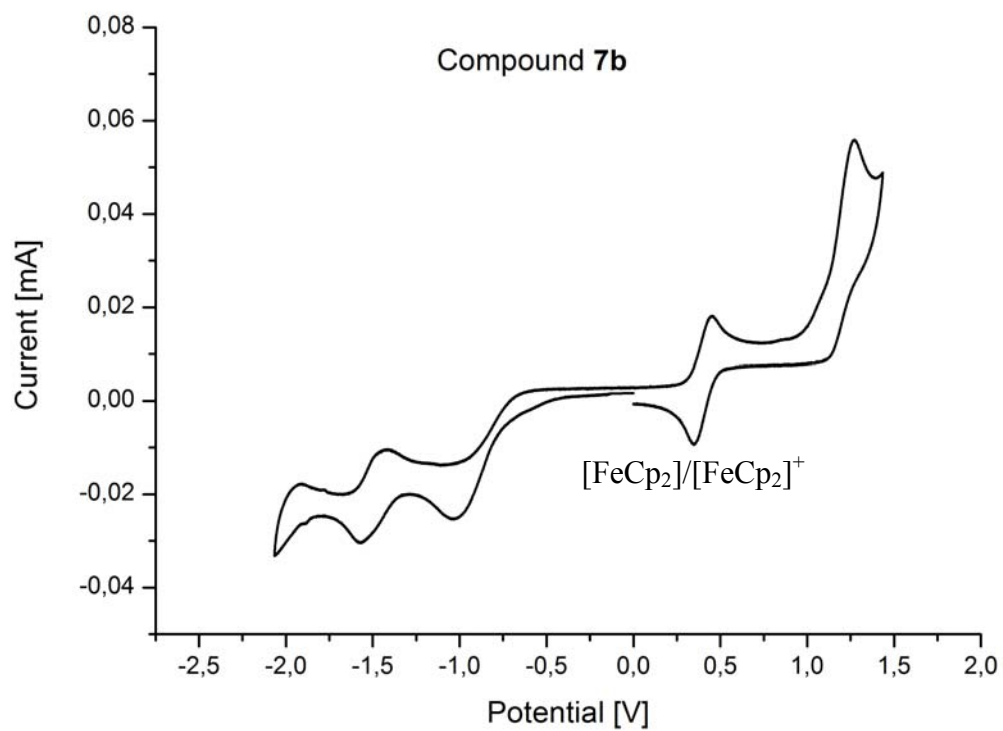
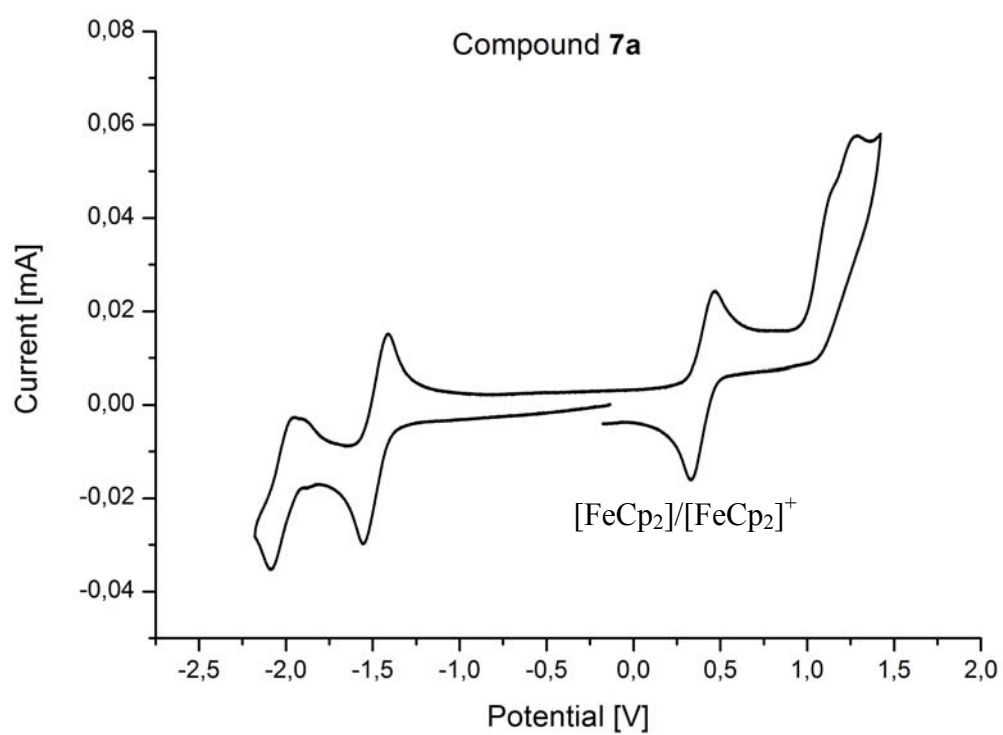
The cyclic voltammetry measurements were performed in 0.1 mol/L tetra-*n*-butylammonium hexafluorophosphate (TBAPF₆) solution in dry THF using a glassy carbon working electrode, a platinum wire as counter electrode and a silver wire as quasi reference electrode. Cyclic voltammetry was carried out under nitrogen atmosphere with a VMP2 from Princeton applied research at a potential scan rate of 20 mV/s. All compounds were measured in solution and ferrocene was added as internal standard in a second measurement.

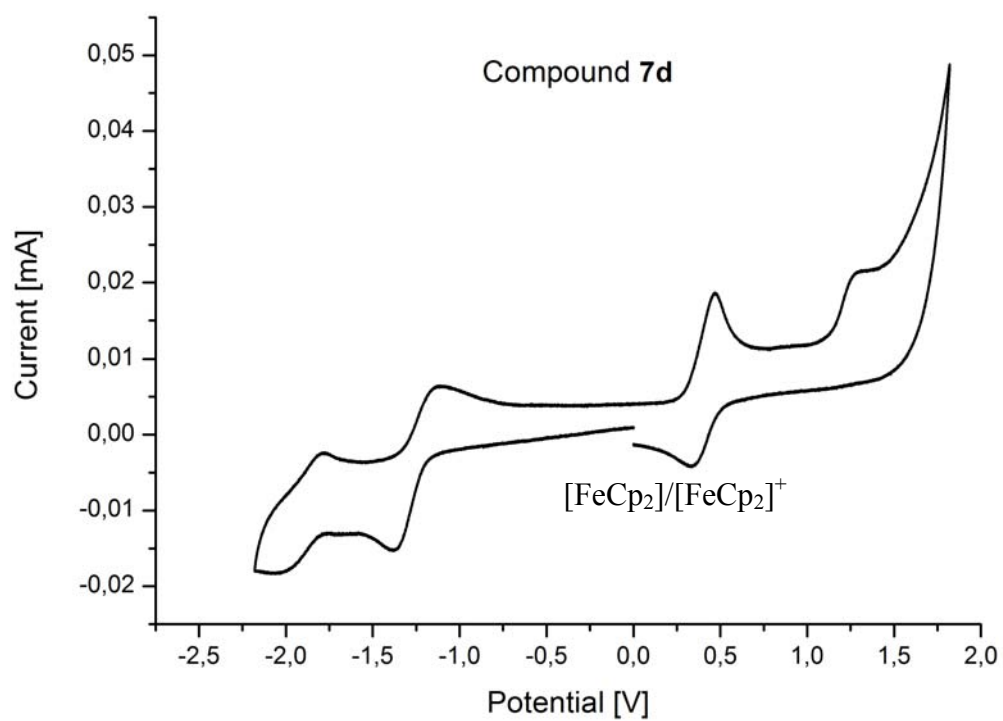
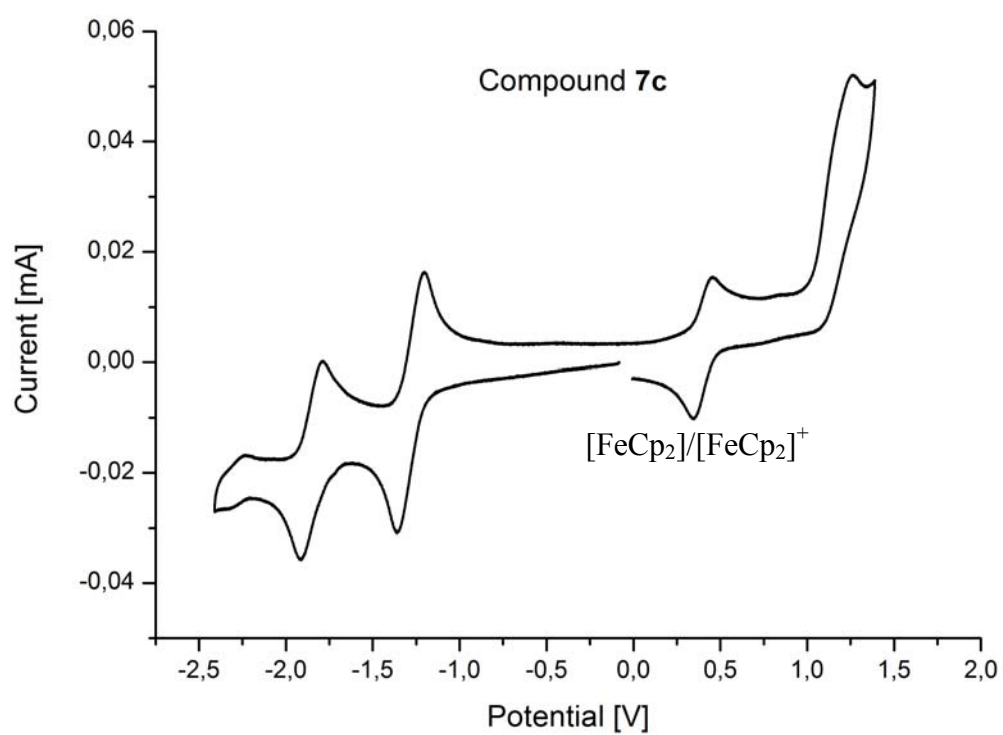
The cyclic voltammograms were calibrated by the formal potential of ferrocene which is 0.4 V versus SCE⁷. Using the equation from Leeuw et al.⁸ ($E_{\text{LUMO}} = -(E_{\text{onset,red}} + 4.4)$ and $E_{\text{HOMO}} = -(E_{\text{onset,ox}} + 4.4)$) the HOMO- and LUMO-energies were calculated from the onset potentials of the first reduction and the oxidation wave (vs SCE). Furthermore the difference of the onset potentials was used to calculate the HOMO-LUMO gap ($E_{\text{gap,CV}} = E_{\text{onset,ox}} - E_{\text{onset,red}}$)⁹.

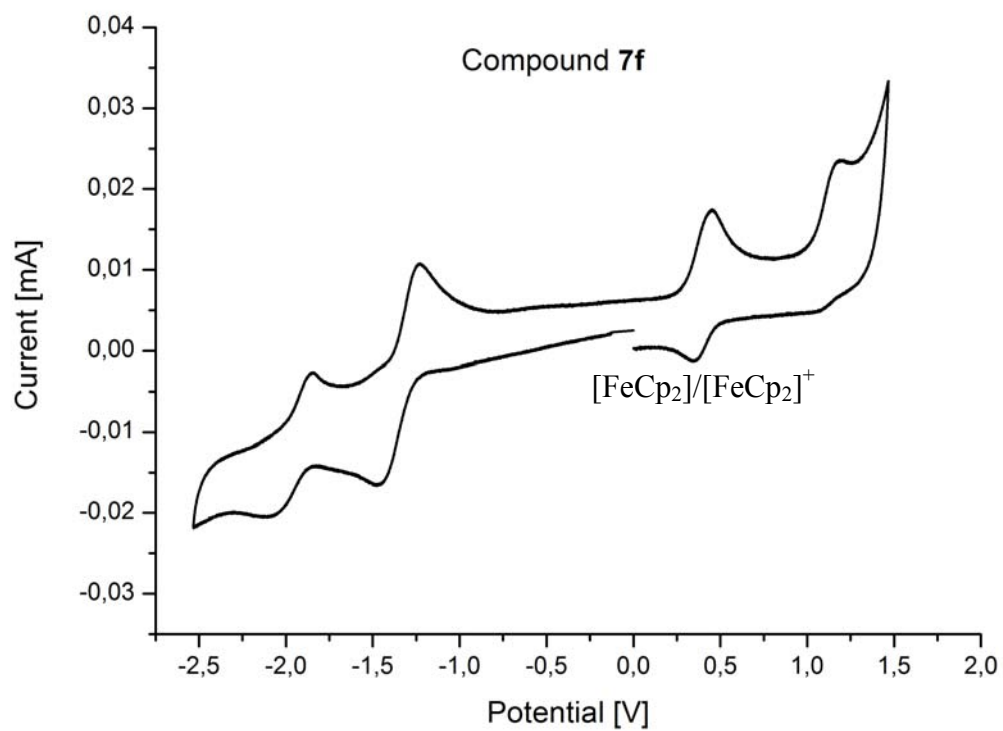
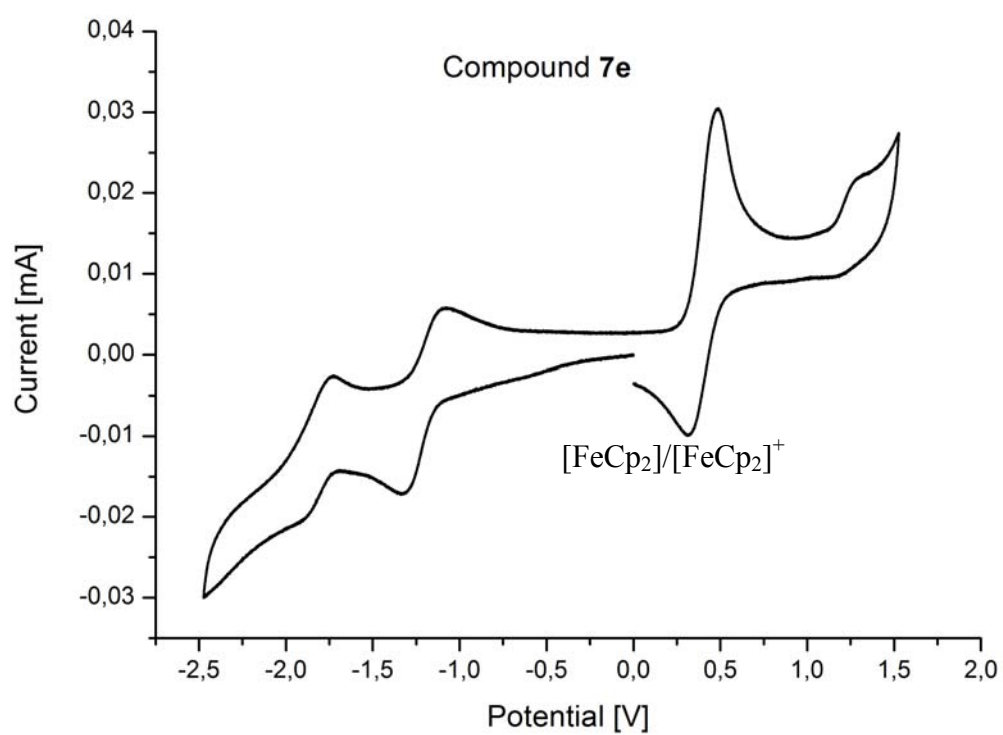
If no oxidation could be observed in the cyclic voltammogram, the HOMO-energy was calculated from the LUMO-energy and the optical band gap predicted from the UV-VIS measurements $E_{\text{HOMO}}^* = E_{\text{LUMO}} - \Delta E_{\text{gap,opt}}$.

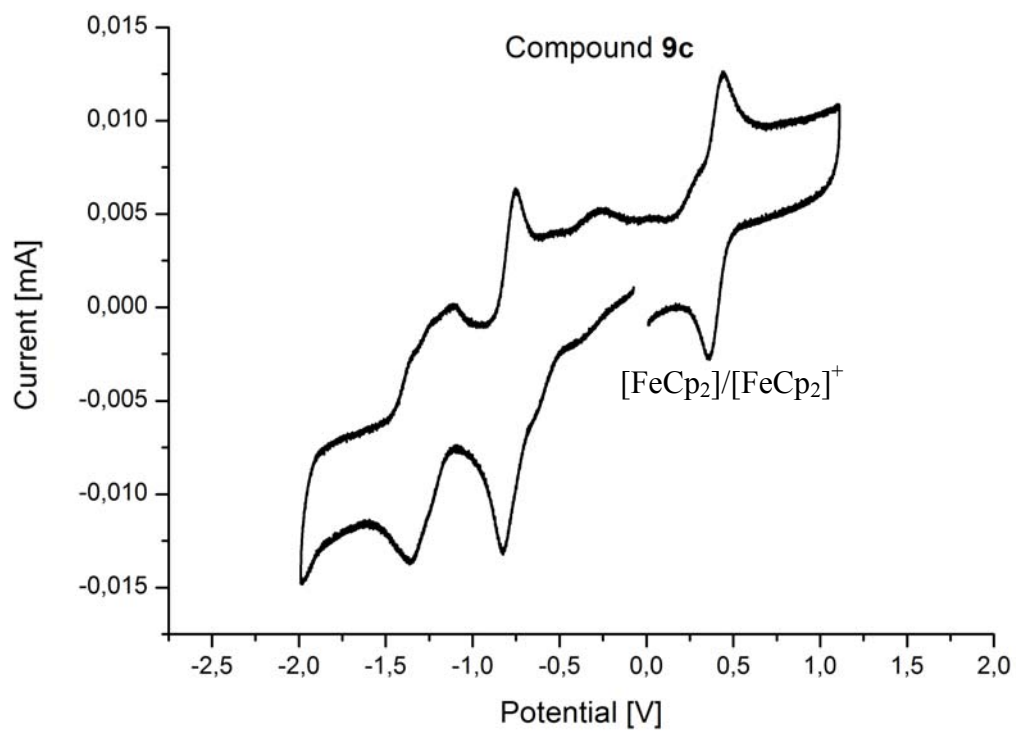
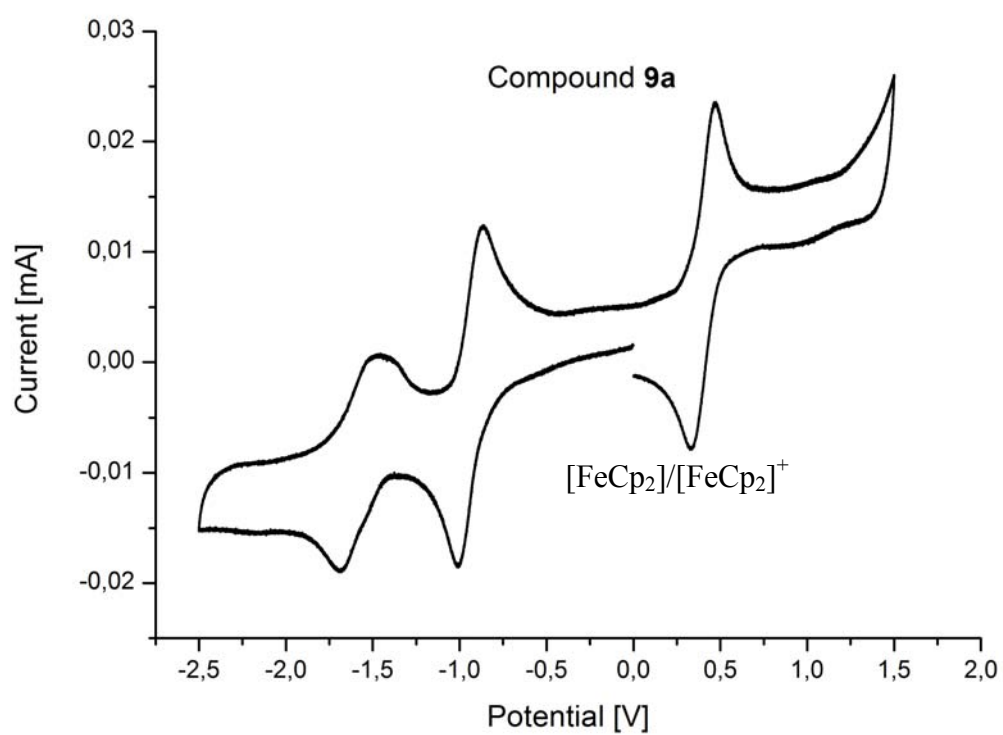
UV-VIS spectra were recorded in 0.01 mmol/L solutions of the compounds in THF.

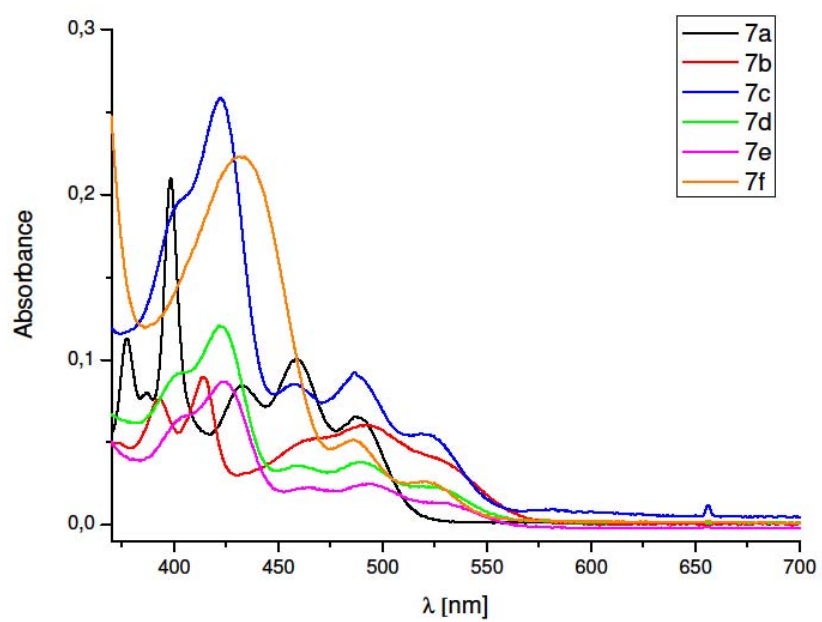
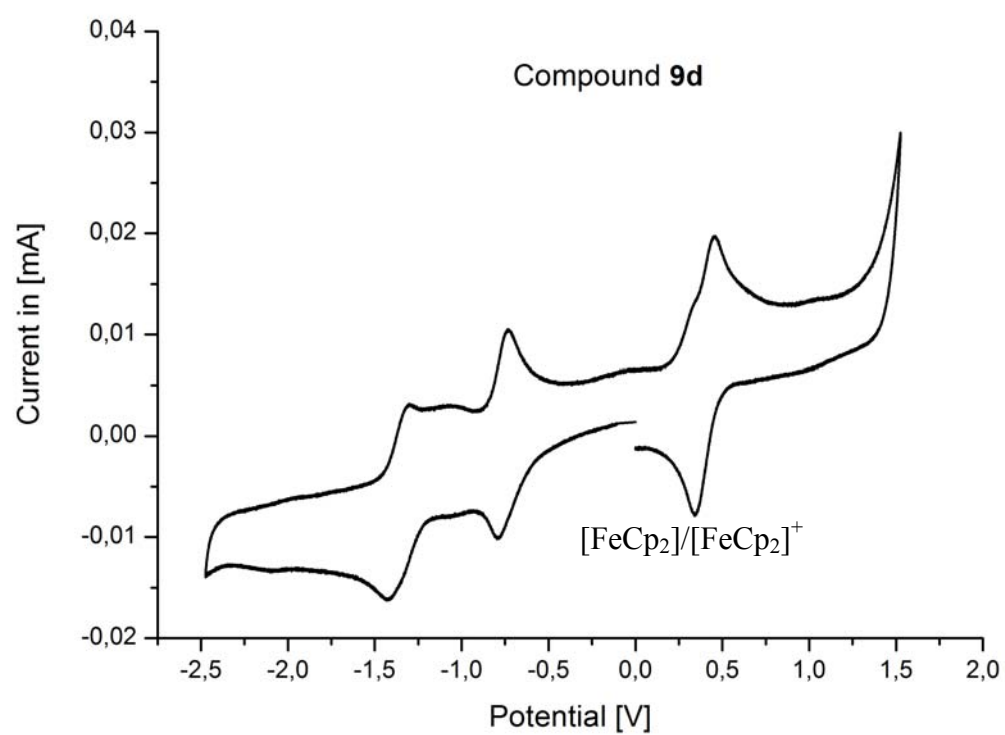
Compound	$E_{\text{onset,red}}$ [V]	$E_{\text{onset,ox}}$ [V]	LUMO [eV]	HOMO [eV]	$\Delta E_{\text{gap,CV}}$ [eV]	$\lambda_{\text{max,onset}}$ [nm]	$\Delta E_{\text{gap,opt}}$ [eV]
7a	-1.39	0.99	-3.01	-5.39	2.38	514	2.41
7b	-0.74	1.08	-3.66	-5.85*	1.82	567	2.18
7c	-1.21	1.03	-3.19	-5.43	2.24	555	2.23
7d	-1.19	1.12	-3.21	-5.52	2.31	560	2.21
7e	-1.15	1.14	-3.25	-5.54	2.29	563	2.20
7f	-1.24	1.00	-3.16	-5.40	2.24	552	2.25
9a	-0.86	-	-3.54	-6.07*		491	2.53
9c	-0.65	-	-3.75	-6.08*		532	2.33
9d	-0.58	-	-3.82	-6.12*		538	2.30

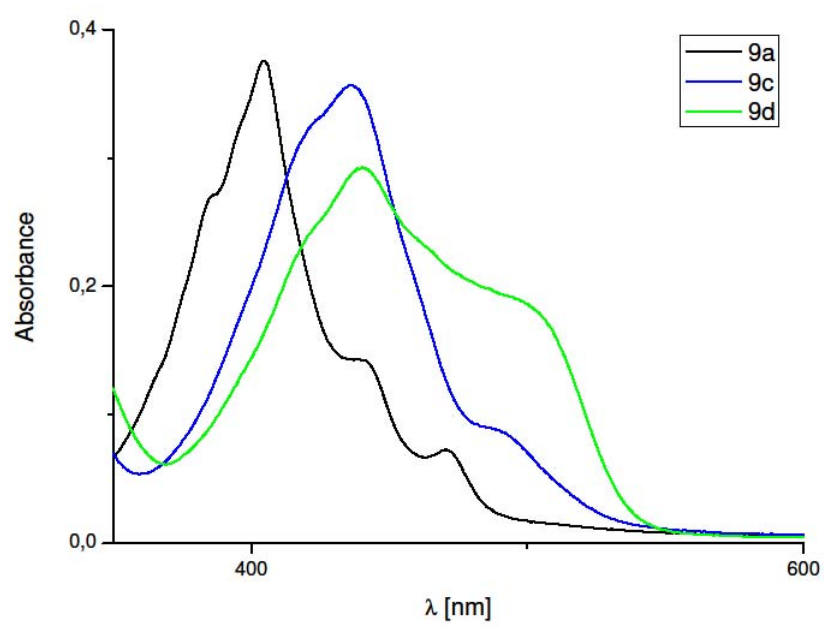








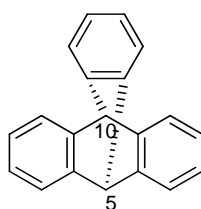




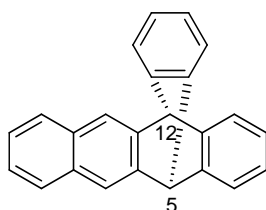
Validation of the calculated chemical shifts

To validate the calculated chemical shifts, the chemical shifts for structurally similar molecules were calculated and compared with their reported chemical shifts. The molecules were Triptycene¹⁰ and several molecules from a publication by Lee et al.¹¹. The calculated chemical shifts of the bridge-head protons and carbon atoms were then compared with their experimental value as reported in the literature^{10,11}.

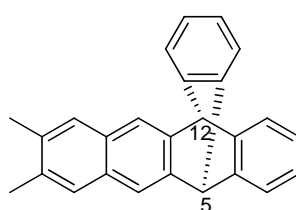
It should be noted that, for ¹H, the calculations are able to predict the general trend of the chemical shift values only. In the case of the bridge-head protons of oxygen-bound carbon atoms, the accuracy is quite low. This might be due to the small differences between the chemical environments of the bridge-head protons. On the other hand, the results for ¹³C show both the correct general trend and a high accuracy. We therefore rely on the ¹³C shifts for the discussion in the paper.



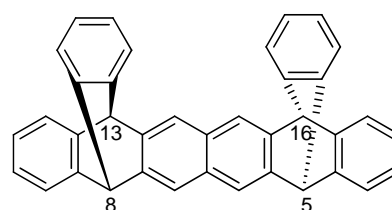
Triptycene



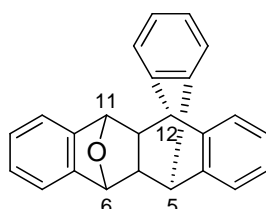
Lee-2b



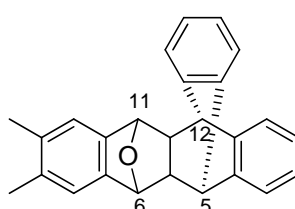
Lee-2d



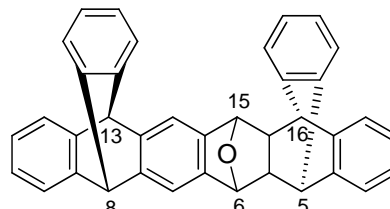
Lee-2e



Lee-8b



Lee-8d

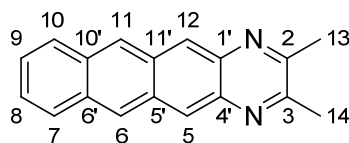


Lee-8e

Molecule	position	¹ H [ppm]		¹³ C [ppm]	
		calc.	exp.	calc.	exp.
Triptycene	5/10	5.43	5.38	56.4	54.1
Lee-2b	5/12	5.38	5.56	56.1	53.7
Lee-2d	5/12	5.33	5.53	56.1	53.7
Lee-2e	5/8/12/13	5.43	5.44	56.0	53.7
Lee-8b	5/12	4.38	4.42	49.8	47.4
	6/11	4.58	4.93	80.2	81.2
Lee-8d	5/12	4.58	4.40	49.7	47.5
	6/11	4.58	4.88	80.0	81.1
Lee-8e	5/16	4.33	4.15	49.8	47.2
	6/15	4.50	4.61	79.9	80.9
	8/13	5.18	5.33	56.7	54.2

All chemical shifts

We used the following nomenclature:



This nomenclature is independent of whether the compound is a dimer, a peroxide or a quinone. For example, in the case of the quinone **19a**, the positions 5/12 belong to carbonyl groups. Thus, there are no protons at the 5/12 position of **19a**, leaving an empty entry in the corresponding field.

In the case of unsymmetric dimers (**20e**, **20f**, **17c**, **17d**, **17e**, **17f**, **17i**, **17j**), the molecule is treated as if it would consist of an upper and a lower half. For example, the dimer **20e** is formed by a connection of the 5/12 position of one molecule with the 7/10 position of another molecule. Therefore, the corresponding chemical shifts of the bridge head atoms can be found in the column of 7/10 for the “upper” half and in the column of 5/12 for the “lower” half.

Molecule		¹ H chemical shift [ppm]				¹³ C chemical shift [ppm]							
		8/9	7/10	5/12	13/14	8/9	7/10	6'/10'	5'/11'	5/12	1'/4'	2/3	13/14
9a	calc.	7.20	8.25	8.56	2.46	129.4	132.0	146.5	144.0	130.7	142.3	153.7	22.1
	ass.	7.78	8.20	8.94	2.77	131.3	129.9	143.7	141.8	128.0	140.0	155.4	23.9
18a	calc.	7.40	7.85	5.08	2.35	129.9	131.6	144.2	151.9	81.5	150.6	154.0	22.0
	ass.									81.5			
18b	calc.	6.79	4.78	8.20	2.48	137.4	76.8	152.3	142.4	130.9	143.2	153.9	23.4
19a	calc.	7.45	8.15		2.52	132.5	133.6	145.3	144.4	174.8	143.2	158.0	22.8
	ass.	8.01	8.48		2.84	133.4	130.4	143.4	142.9	178.6	142.0	159.2	22.3
19b	calc.	6.69		8.56	2.47	138.0	178.7	143.6	143.0	134.0	144.5	155.7	22.2
20a	calc.	6.24	4.23	8.15	2.46	137.9	48.7	159.2	141.8	130.0	143.1	153.3	23.4
20b	calc.	6.67	4.31	7.90	2.32	138.9	51.0	157.2	141.4	130.0	143.1	152.8	23.2
20c	calc.	7.30	7.70	4.88	2.04	129.0	131.0	143.1	157.1	54.0	154.2	151.6	21.5
	ass.	7.59	7.88	5.35	2.10	128.8	127.8	138.9	154.4	51.8	150.3	149.4	20.4
20d	calc.	7.17	7.60	4.88	2.20	129.1	130.9	143.0	156.6	54.2	154.8	151.5	21.6
	ass.	7.42	7.72	5.36	2.32	128.8	127.7		153.8	51.8	150.9	149.2	20.5
20e upper	calc.	6.39	4.53	7.95	2.31	137.6	49.8	157.1	141.4	130.2	143.2	152.9	23.2
20e lower	calc.	7.15	7.55	4.68	2.33	129.1	130.8	142.8	156.4	54.1	156.5	151.4	21.7
20f upper	calc.	6.34	4.50	8.05	2.40	137.7	49.3	157.7	141.6	130.2	143.3	153.0	23.3
20f lower	calc.	7.40	7.80	4.68	2.01	129.1	130.9	143.3	158.6	53.7	154.2	151.6	21.5

Molecule		¹ H chemical shift [ppm]					¹³ C chemical shift [ppm]								
		8/9	7/10	6/11	5/12	13/14	8/9	7/10	6'/10'	6/11	5'/11'	5/12	1'/4'	2/3	13/14
7a	calc.	6.95	8.25	8.81	8.61	2.41	125.4	129.6	134.6	128.5	134.9	129.2	140.8	153.0	23.8
	ass.	7.31	7.92	8.60	8.66	2.61	125.0	127.7	131.6	126.1	131.0	126.2	137.7	154.5	22.4
16a	calc.	7.25	7.90	7.75	5.33	2.25	127.0	129.4	136.3	123.5	136.9	79.6	152.7	151.5	21.7
	ass.	7.39	7.77	7.85	6.15		126.3	127.7	132.8	122.7	133.8	80.1	149.2	150.3	20.5
16b	calc.	7.15	7.25	5.28	7.60	2.45	129.3	124.9	142.2	77.8	140.6	124.1	143.5	152.9	22.9
	ass.	7.18	7.37	6.18	7.80	2.55	127.4	123.1	138.1	78.1	138.3	122.2	140.5	153.3	21.7
16c	calc.	6.74	4.93	7.95	8.30	2.46	136.6	74.6	137.2	121.6	135.4	129.1	141.7	152.9	23.3
15a	calc.	7.25	8.15	8.86		2.48	129.2	131.9	138.0	130.7	130.9	177.0	143.6	157.3	22.7
	ass.	7.63	8.10	8.78		2.65	129.1	129.6	134.9	128.5	129.6	180.2		157.5	21.5
	exp.	7.62	8.10	8.78		2.65	129.0	129.5	134.9	128.5	129.6	180.1	143.2	157.5	21.4
15b	calc.	7.35	8.46		8.61	2.48	134.4	130.0	135.6	178.5	133.5	131.9	145.7	155.6	23.3
	ass.	7.77	8.25		8.70	2.67	133.7	126.7	134.0	181.0	132.1	128.4	142.7	157.2	22.2
	exp.	7.77	8.24		8.69	2.66	133.6	126.6	134.0	181.1	132.1	128.3	142.8	157.2	22.2
15c	calc.	6.54	0.00	8.86	8.56	2.37	138.2	180.7	129.1	131.0	136.3	133.1	143.0	154.7	23.4
17a	calc.	6.24	4.38	8.00	8.25	2.44	138.5	49.7	144.0	124.5	135.4	127.8	141.5	152.1	23.3
17b	calc.	6.54	4.33	7.85	8.00	2.33	138.4	51.3	142.7	125.8	135.0	127.7	141.4	151.9	23.2
17c upper	calc.	6.64	7.05	4.93	7.65	2.45	127.8	129.1	146.2	55.3	146.8	126.7	143.0	151.9	22.9
17c lower	calc.	6.32	4.58	7.70	8.05	2.35	138.1	49.9	143.1	125.7	135.4	127.7	141.7	151.8	23.1
17d upper	calc.	7.00	7.25	5.08	7.45	2.25	127.8	127.8	147.0	55.3	145.4	127.8	142.5	151.7	22.7
17d lower	calc.	6.34	4.58	7.70	7.95	2.30	137.7	50.1	142.7	125.9	135.3	127.7	141.7	151.7	23.1
17e upper	calc.	7.00	7.55	7.60	4.63	2.30	125.9	128.3	135.3	127.2	141.8	54.6	157.7	149.9	21.6
17e lower	calc.	6.24	4.53	7.90	8.05	2.38	136.9	49.3	142.4	125.8	135.1	127.8	141.3	152.0	23.2
17f upper	calc.	7.20	7.80	7.75	4.68	1.99	126.0	128.5	135.8	126.0	143.1	55.1	156.4	149.7	21.4
17f lower	calc.	6.29	4.53	7.90	8.15	2.43	138.1	48.8	142.1	125.6	135.2	127.9	141.3	152.1	23.3
17g	calc.	6.72	7.07	5.12	7.50	2.38	127.8	129.0	145.9	54.9	145.7	127.6	142.7	151.7	22.8
	ass.			4.83-4.95						52.0-53.5					
17h	calc.	6.84	7.05	5.03	7.50	2.31	127.9	128.9	146.1	55.1	145.5	127.9	142.6	151.7	22.7
	ass.			4.83-4.95						52.0-53.5					
17i upper	calc.	7.05	7.60	7.60	4.78	2.16	125.8	128.4	135.5	127.2	141.8	55.0	156.4	149.9	21.5
	ass.				4.83-4.95							52.0-53.5			
17i lower	calc.	6.84	7.10	5.03	7.50	2.30	127.9	129.0	145.4	54.2	145.3	127.9	142.5	151.8	22.7
	ass.			4.83-4.95						52.0-53.5					
17j upper	calc.	7.15	7.70	7.60	4.83	2.04	125.9	128.4	135.7	126.9	142.0	55.0	156.1	149.9	21.4
	ass.				4.83-4.95							52.0-53.5			
17j lower	calc.	6.69	7.07	5.03	7.50	2.40	127.8	129.1	145.9	54.2	145.0	127.8	142.8	151.9	22.8
	ass.			4.83-4.95						52.0-53.5					
17k	calc.	7.08	7.63	7.69	4.92	2.01	126.8	128.9	136.3	126.8	141.0	54.1	156.6	149.3	21.3
	ass.				4.83-4.95							52.0-53.5			
17l	calc.	7.05	7.60	7.60	4.83	2.17	125.9	128.3	135.4	127.2	141.8	54.3	155.7	150.2	21.5
	ass.				4.83-4.95							52.0-53.5			

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