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Supporting Information

69451 Weinheim, Germany

Title: Banana-shaped oligo(aryleneethynylene)s: synthesis and light-emitting characteristics.

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Experimental Section

Synthesis of 5. Bromine (1 equiv) in CH_2Cl_2 (0.4 ml/mmol) was added dropwise to a solution of 3-iodo-4-methoxyphenol **8**[17] in CH_2Cl_2 (2 ml/mmol) at 0°C and stirred at this temperature for an additional 30 min. The mixture was poured into ether and water, and the organic layer was washed with water, aqueous sodium thiosulfate solution and brine. Drying with $MgSO_4$ and evaporation of the solvent yielded 2-bromo-5-iodo-4-methoxy-phenol (92%). To the solution of the obtained product in acetone (5 ml/ mmol) was added K_2CO_3 (2 equiv) and iodomethane (3 equiv). After reflux overnight, the reaction mixture cooled down to room temperature. Then the mixture was concentrated, poured into water and $CHCl_3$. The separated aqueous phase was extracted with $CHCl_3$. The organic fractions were dried over $MgSO_4$ and evaporated. Chromatography on SiO_2 (eluent: benzene/hexane) yielded **10** (93%). $[Pd(PPh_3)_2Cl_2]$ (0.04 equiv) and CuI (0.02 equiv) were added to a solution of **10** and trimethylsilylacetylene (1.2 equiv) in Et_3N (5 ml/mmol) at room temperature. The mixture was stirred for 3 h under Ar at the same temperature and then the solvent was removed. The residue was purified by column chromatography on SiO_2 (eluent: hexane/AcOEt) to give 2-bromo-4-methoxy-5-(2-tri-methylsilylethynyl)anisole (97%). $[Pd(PPh_3)_2Cl_2]$ (0.04 equiv) and CuI (0.02 equiv) were added to a solution of the obtained product and triisopropylsilylacetylene (1.2 equiv) in Et_3N (5 ml/mmol) at room temperature. The mixture was refluxed for 12 h under Ar. After the reaction mixture cooled down to room temperature, the solvent was removed. The residue was purified by column chromatography on SiO_2 (eluent: hexane/AcOEt) to give **11** (97%). Compound **11** was dissolved in MeOH/THF (4:3; 7 ml/mmol). K_2CO_3 (3 equiv) was added, and the reaction mixture was stirred

at room temperature for 14 h. The mixture was poured into ether and water. The organic layer was washed with water and brine, and dried over $MgSO_4$. Evaporation of the solvent and chromatography on SiO_2 (eluent: hexane/AcOEt) gave 2-ethynyl-4-methoxy-5-(2-triisopropylsilylethynyl)anisole (91%). $[Pd(PPh_3)_2Cl_2]$ (0.04 equiv) and CuI (0.02 equiv) were added to a solution of 2-bromopyridine in Et_3N/THF (4:3; 5 ml/mmol) at room temperature. While the mixture was stirred under Ar at room temperature, a solution of the obtained product (1.1 equiv) in THF (5 ml/mmol) was added. After addition, the reaction mixture was stirred for 12 h at room temperature and then the solvent was removed. The residue was purified by column chromatography on SiO_2 (eluent: $CHCl_3$) to give 4-methoxy-2-[2-(2-pyridyl)-ethynyl]-5-(2-triisopropylsilyl-ethynyl)anisole (77%). A solution of Bu_4NF in THF (4 equiv) was added to a solution of the obtained product in THF (3 ml/mmol). The mixture was stirred for 1 h at room temperature and then poured into ether and water. The organic layer was washed with water and brine, and dried over $MgSO_4$. Evaporation of the solvent and chromatography on SiO_2 (eluent: $CHCl_3$) gave **12** (74%). $[Pd(PPh_3)_2Cl_2]$ (0.04 equiv) and CuI (0.02 equiv) were added to a solution of 2,6-dibromopyridine in Et_3N (5 ml/mmol) at room temperature. While the mixture was stirred under Ar at room temperature, a solution of **12** (3 equiv) in THF (2 ml/mmol) was added to the flask. After addition, the reaction mixture was refluxed for 6 h. The reaction mixture cooled down to room temperature and then the solvent was removed. The residue was purified by column chromatography on SiO_2 (eluent: $CHCl_3$/AcOEt) followed by recrystallization from benzene to give the desired product **5** (65%).

Synthesis of 6. $[Pd(PPh_3)_2Cl_2]$ (0.02 equiv) and CuI (0.01 equiv) were added to a solution of 2,6-dibromopyridine in Et_3N (10 ml/mmol) at room temperature. While the mixture was stirred under Ar at room temperature, a solution of **9** (1.1 equiv) in Et_3N (3 ml/mmol) was added. After addition, the reaction mixture was stirred for 2 h at room temperature. Then trimethylsilyl-acetylene (1.2 equiv) was added and the mixture was refluxed for 5 h. After the reaction mixture cooled down to room temperature, the solvent was removed. The residue was purified by column chromatography on SiO_2 (eluent: CH_2Cl_2) to give 4-methoxy-5-2-triisopropylsilylethynyl)-2-{2-[6-(2-trimeth-ylsilylethynyl)pyridyl]ethynyl}anisole (37%). The obtained product was dissolved in an approximate 10:1 mixture of $CHCl_3$ and MeOH with 2M aqueous KOH (≈ 10 equiv), and the reaction mixture was stirred for 30 min at room temperature and poured into $CHCl_3$ and water. The organic fractions were then dried over $MgSO_4$ and evaporated. Chromatography on SiO_2 (eluent: CH_2Cl_2) yielded **13** (82%). On the other hand, a mixture of 2-iodo-4-methoxyanisole prepared from 2-iodo-4-methoxyphenol **8**[17], iodine (0.8 equiv), iodic acid (0.4 equiv), sulfuric acid (0.04 ml/mmol), CCl_4 (0.2 ml/mmol), acetic acid (0.48 ml/mmol) and water (0.24 ml/mmol) was refluxed for 24 h. After cooling to room temperature, the mixture was poured into ether and water. The organic layer was washed with water, aqueous sodium thiosulfate, 10% aqueous sodium hydroxide, water and brine. Drying with $MgSO_4$ and evaporation of the solvent gave the crude product, which was recrystallized from MeOH to yield **14** (76%). $[Pd(PPh_3)_2Cl_2]$ (0.04 equiv) and CuI (0.02 equiv) were added to a solution of **14** in Et_3N (5 ml/mmol) at room temperature. While the mixture was stirred under Ar at room temperature, a solution of **13** (3 equiv) in THF (2 ml/mmol)

was added. After addition, the reaction mixture was refluxed for 4 h. The reaction mixture cooled down to room temperature and then the solvent was removed. The residue was purified by column chromatography on SiO_2 (eluent: $CHCl_3$/AcOEt) followed by recrystallization from benzene to give the desired product **6** (28%).

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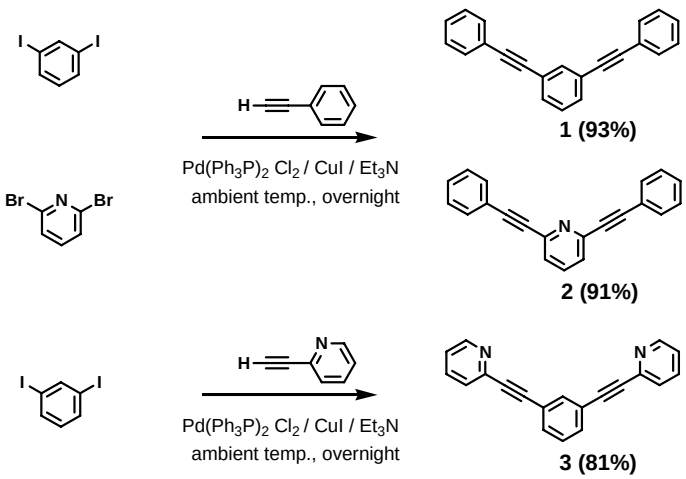
[17] S. Höger, *Liebigs Ann./Recueil*, **1997**, 273-277.

Synthesis of Banana-shaped OAEs (1 – 3)



NMR and HR MS (FAB) Data of Banana-shaped OAEs

1: ^{1}H NMR ($CDCl_3$): δ = 7.33-7.38 (m, 7H), 7.42-7.56 (m, 6H), 7.72 (bs, 1H); ^{13}C NMR ($CDCl_3$): δ = 88.52, 89.94, 122.98, 123.60, 128.36, 128.42, 128.45, 131.25, 131.50, 131.63, 134.58.

HR MS (FAB, positive ion mode) calcd 278.1096, found 278.1098.

2: ^{1}H NMR ($CDCl_3$): δ = 7.35-7.40 (m, 6H), 7.47 (d, J=7.8 Hz, 2H), 7.58-7.63 (m, 4H), 7.68 (dd, J=7.7, 7.8 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ = 88.25, 89.62, 122.08, 126.20, 128.36, 129.07, 132.08, 136.40, 143.77.

HR MS (FAB, positive ion mode) calcd 280.1126, found 280.1140.

3: ^{1}H NMR ($CDCl_3$): δ = 7.26 (dd, J=4.8, 7.8 Hz, 2H), 7.37 (t, J=6.0 Hz, 1H), 7.54 (d, J=7.8 Hz, 2H), 7.60 (d, J=6.0 Hz, 2H), 7.70 (t, J=7.8 Hz, 1H), 7.83 (s, 1H), 8.64 (d, J=4.8 Hz, 2H); ^{13}C NMR

($CDCl_3$): δ = 88.01, 89.21, 122.70, 122.93, 127.26, 128.58, 132.38, 135.24, 136.17, 143.14, 150.09.
HR MS (FAB, positive ion mode) calcd 281.1079, found 281.1064.

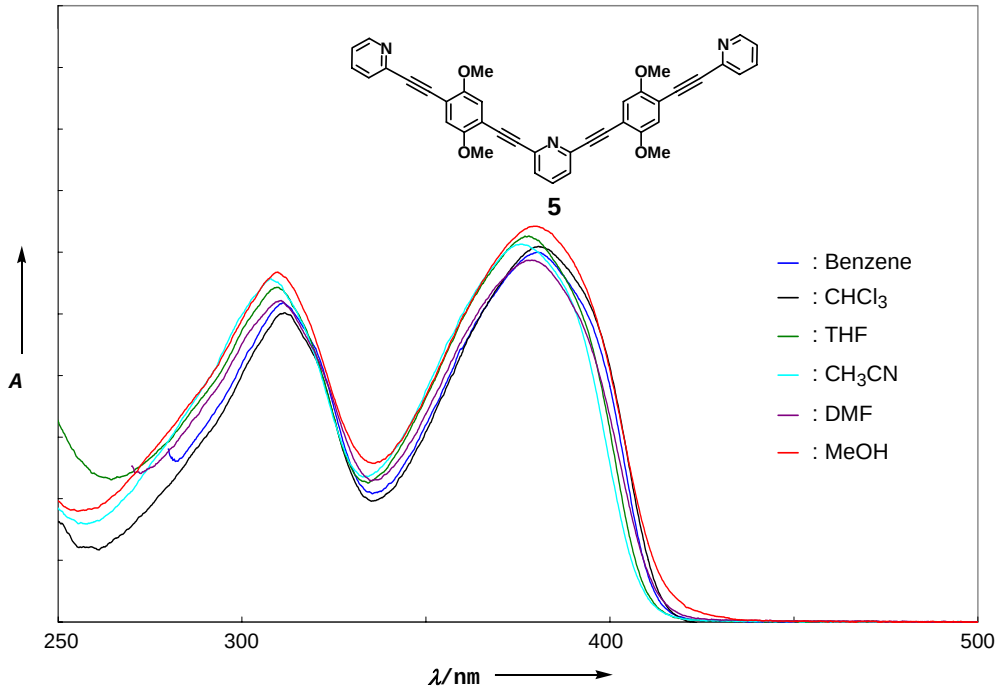
4: ^{1}H NMR ($CDCl_3$): δ = 3.78 (s, 6H), 3.88 (s, 6H), 6.83 (d, J=9.0 Hz, 2H), 6.90 (dd, J=3.3, 9.0 Hz, 2H), 7.13 (d, J=3.3 Hz, 2H), 7.49 (d, J=7.5 Hz, 2H), 7.65 (t, J=7.5 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ = 55.79, 56.38, 86.11, 92.22, 111.72, 112.04, 116.96, 118.16, 126.23, 136.16, 143.87, 153.08, 154.97.
HR MS (FAB, positive ion mode) calcd 400.1549, found 400.1566.

5: ^{1}H NMR ($CDCl_3$): δ = 3.89 (s, 6H), 3.90 (s, 6H), 7.13 (s, 2H), 7.14 (s,2H), 7.24 (dd, J=4.8, 7.5 Hz, 2H), 7.52 (d, J=7.5 Hz, 2H), 7.57 (d, J=7.5 Hz, 1H), 7.69 (t, J=7.5 Hz, 4H), 8.64 (d, J=4.8 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ = 56.38, 56.40, 85.41, 85.92, 93.87, 94.28, 112.87, 113.16, 115.91, 116.00, 122.82, 126.46, 127.27, 136.08, 136.31, 143.29, 143.69, 150.08, 154.16, 154.24.
HR MS (FAB, positive ion mode) calcd 602.2080, found 602.2075.

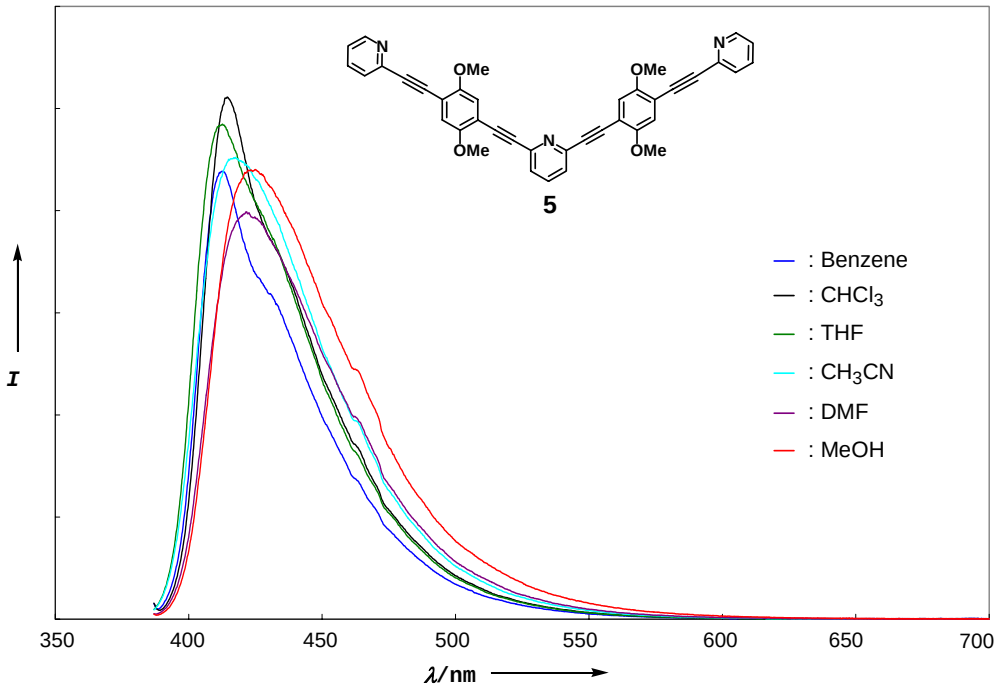
6: ^{1}H NMR ($CDCl_3$): δ = 3.78 (s, 6H), 3.88 (s, 6H), 3.89 (s, 6H), 6.84 (d, J=9.0 Hz, 2H), 6.91 (dd, J=3.0, 9.0 Hz, 2H), 7.13 (d, J=3.0 Hz, 1H), 7.14 (s, 2H), 7.51 (d, J=7.2 Hz, 2H), 7.67 (t, J=7.2 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ = 55.81, 56.39, 85.84, 86.29, 92.15, 93.99, 111.68, 112.04, 113.03, 116.02, 117.02, 118.18, 126.30, 126.45, 136.25, 143.60, 143.98, 153.09, 154.22, 154.99.
HR MS (FAB, positive ion mode) calcd 661.2339, found 661.2337.

Solvent Effect on Absorption and Fluorescence Spectra of Banana-shaped Pentameric Systems (5 and 6)

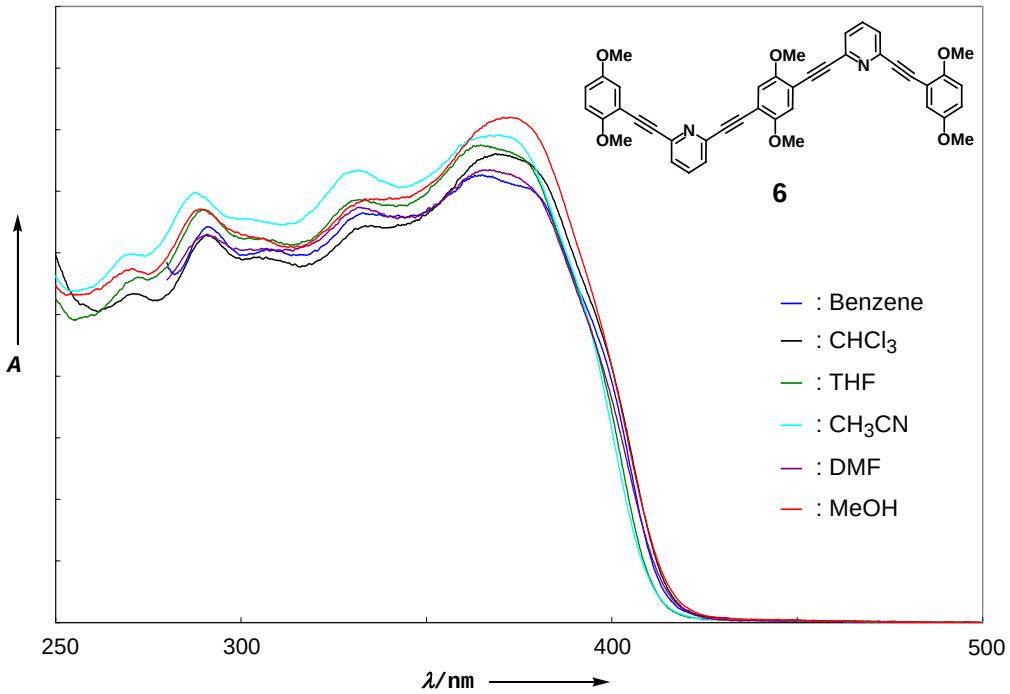
Absorption Spectra of **5** at 295 K



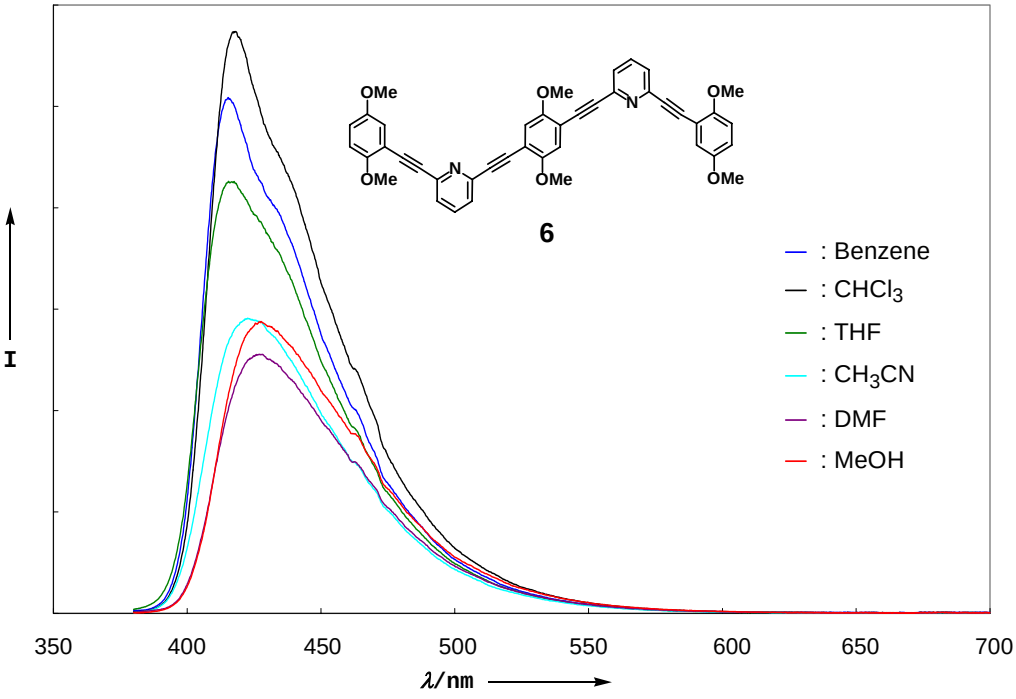
Fluorescence Spectra of **5** at 295 K



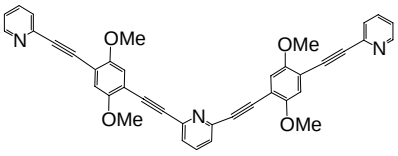
Absorption Spectra of **6** at 295 K



Fluorescence Spectra of **6** at 295 K



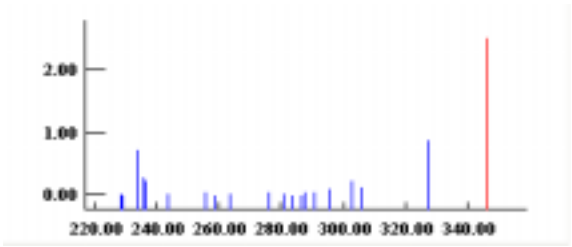
Absorption Spectra by INDO/S and HOMO/LUMO Diagram (AM1) for Banana-shaped Pentameric Systems (5 and 6)



5

H. F. (kcal/mol) = 233.77

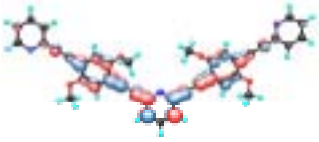
G. N. = 0.42



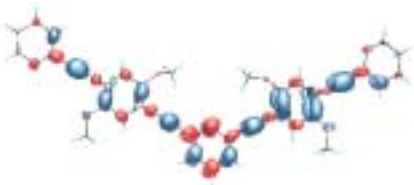
Absorption spectrum of **5** calculated by INDO/S (λ_{abs} = 346 nm, red line)

HOMO (eV) = -8.545

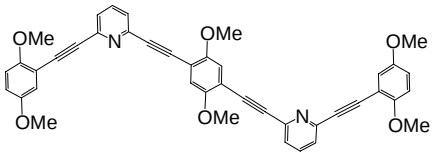
INDO/S difference density distribution of **5**



LUMO (eV) = -1.138



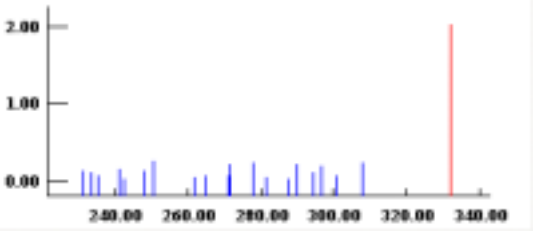
(excitation at 346 nm, calculated λ_{abs})



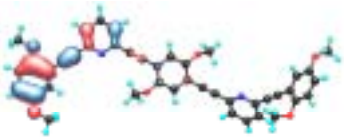
6

H. F. (kcal/mol) = 149.28

G. N. = 1.94

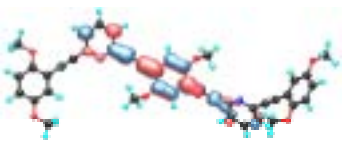


Absorption spectrum of **6** calculated by INDO/S (λ_{abs} = 332 nm, red line)

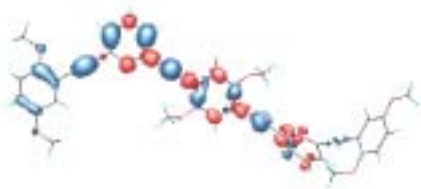


HOMO (eV) = -8.511

INDO/S difference density distribution of **6**

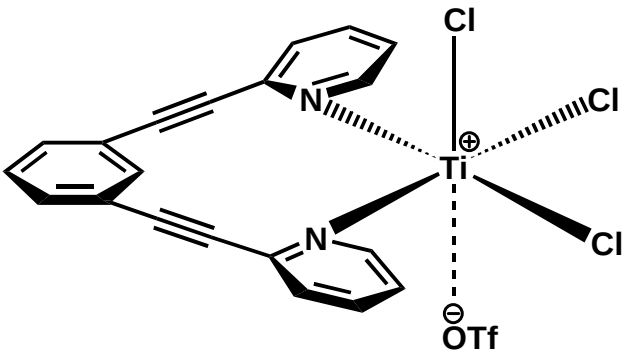


LUMO (eV) = -1.002



(excitation at 332 nm, calculated λ_{abs})

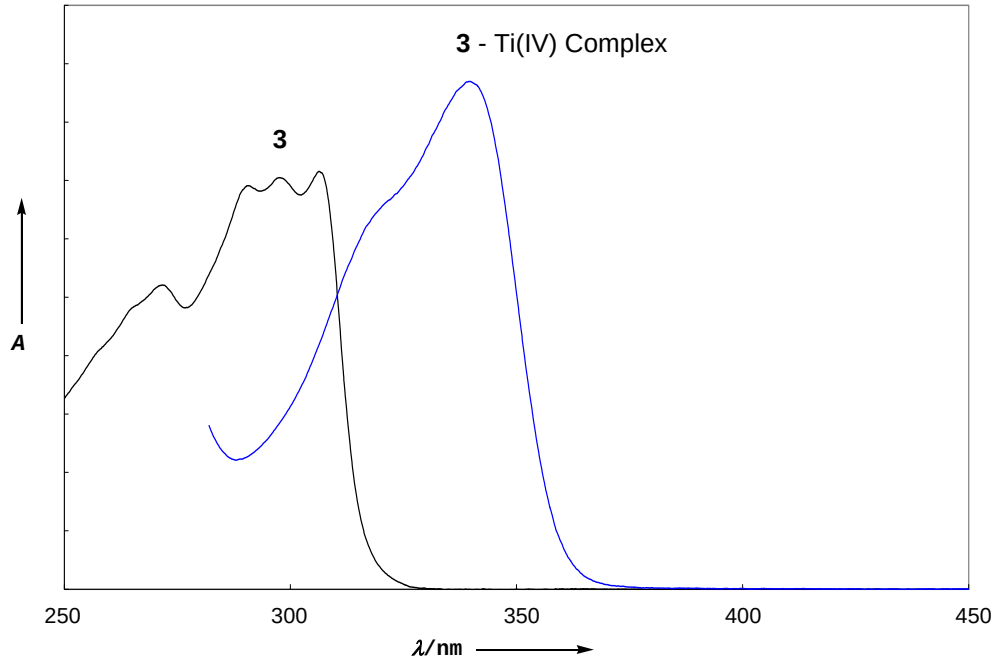
Structure of 3-$TiCl_3$·OTf Complex 18



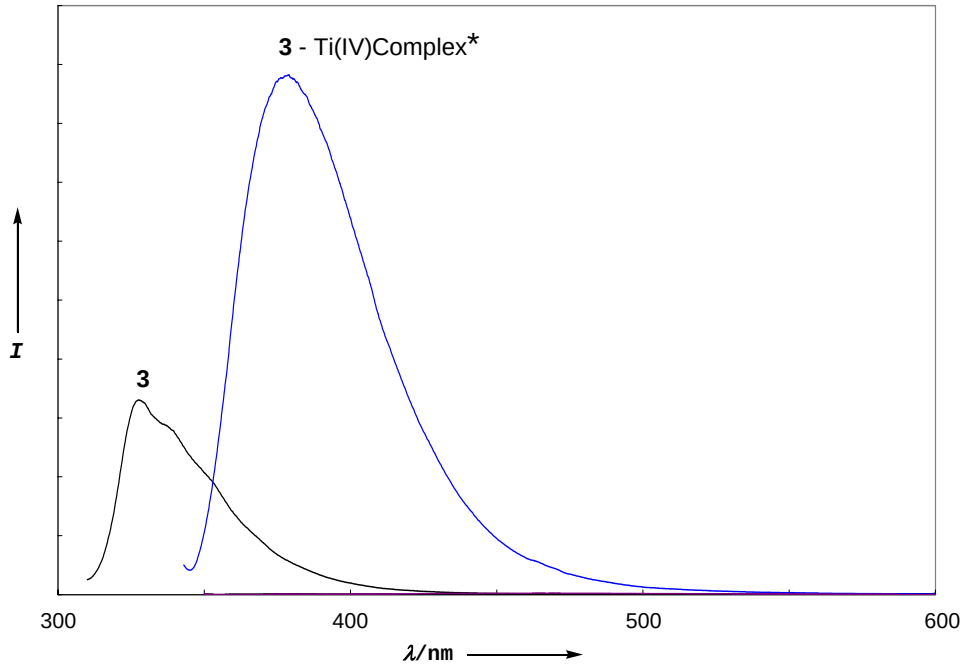
which is abbreviated as 3-Ti(IV)Complex

Absorption and Fluorescence Spectra of 3 and 3-Ti(IV)Complex

Absorption Spectra of **3** and **3**-Ti(IV)Complex in CH_2Cl_2 at 295 K



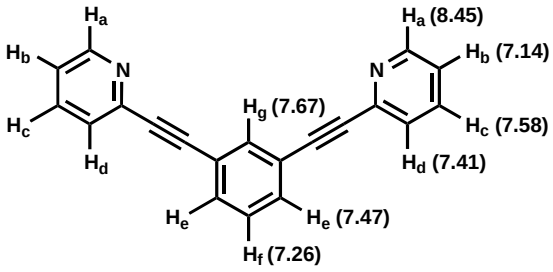
Fluorescence Spectra of **3** and **3**–Ti(IV)Complex in CH_2Cl_2 at 295 K



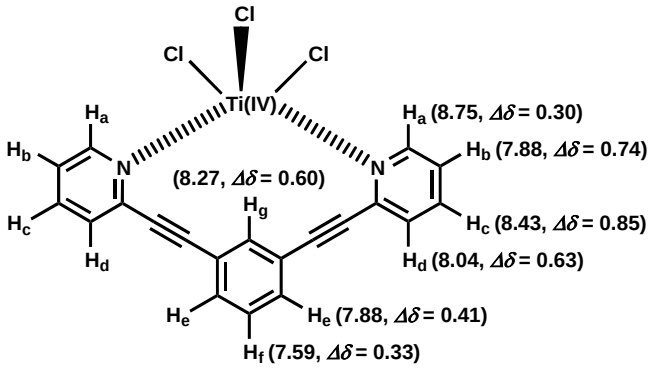
* The solution of **3**–Ti(IV) complex was diluted to one twentieth of the original concentration.

Continuous-variation Method for The Complex Between 3 and $TiCl_3$·OTf in CH_2Cl_2 at 295 K

^{1}H NMR Spectral Data of 3 and 3-Ti(IV)Complex



3



3-Ti(IV) Complex

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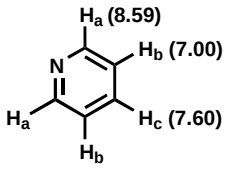
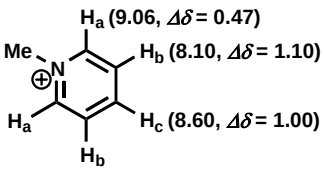
cf. Chemical shift values by ^{1}H NMR caluculation soft
(Advanced Chemistry Development Inc., Toronto, Canada)





FAB MS Data of 3-Ti(IV)Complex

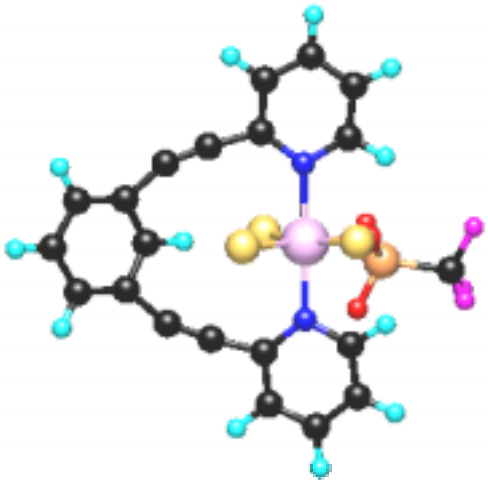
Positive ion mode (matrix: 3-nitrobenzylalchohol):

434($[PBP-TiCl_3]^+$), 281($[PBP+H]^+$), 153($[TiCl_3]^+$)

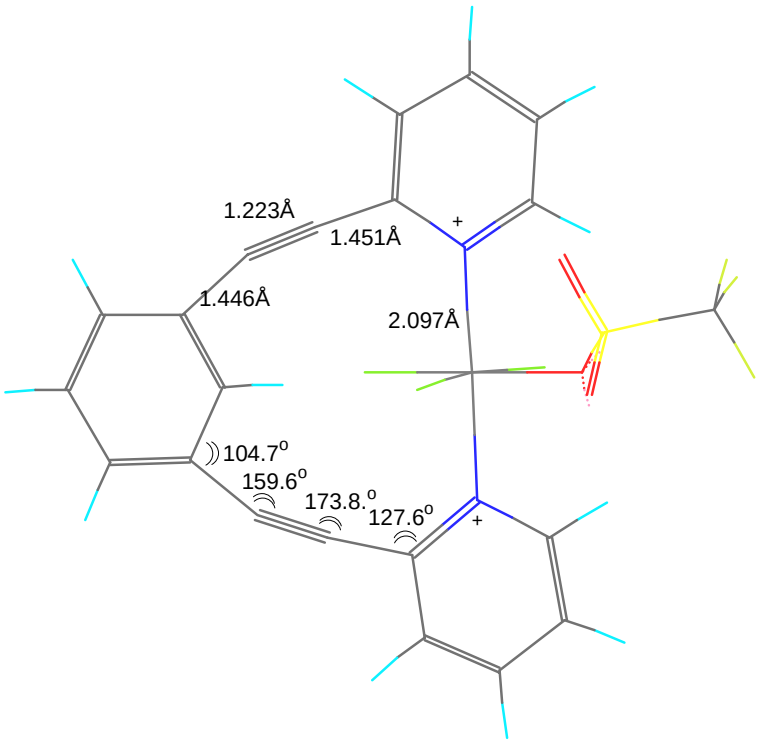
Negative ion mode (matrix: 3-nitrobenzylalchohol): 149($[OTf]^-$)

MM2 Structure

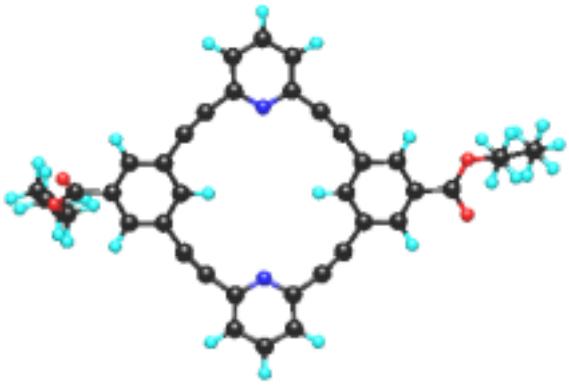
3-Ti(IV)Complex (**18**)



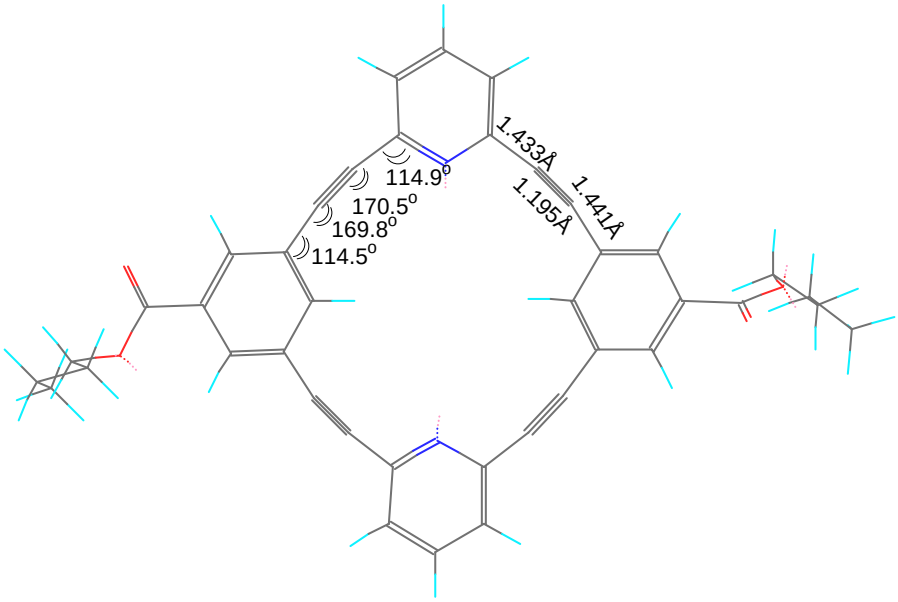
Stretch: 10.9822
Bend: 36.1503
Stretch-Bend: 0.6324
Torsion: -3.2276
Non-1,4 VDW: -2.4413
1,4 VDW: 25.1224
Charge/Charge: 52.7500
Charge/Dipole: 6.7536
Dipole/Dipole: 22.6476
Total: 149.3696



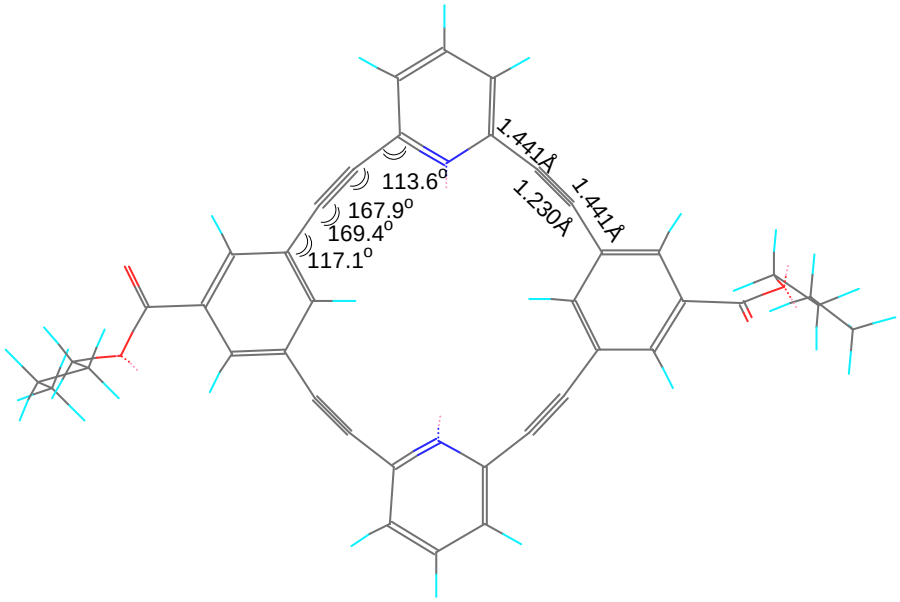
Tetrakis-areneazaarenecyclyne (**20**)



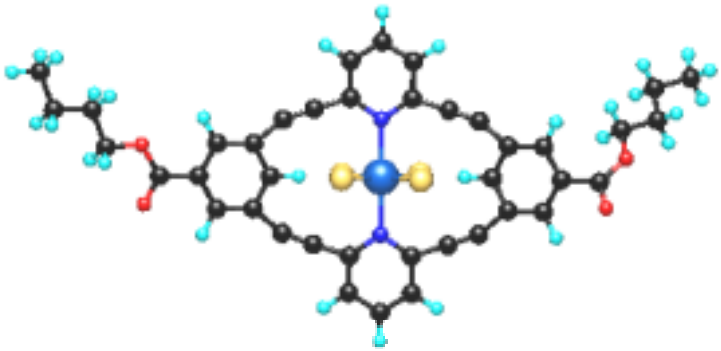
Stretch:	1.8658
Bend:	18.4695
Stretch-Bend:	0.0836
Torsion:	-1.6569
Non-1,4 VDW:	-6.4042
1,4 VDW:	25.5166
Dipole/Dipole:	6.5226
Total:	44.3969



cf. Data obtained from X-ray diffraction analysis



20-Sb(IV)Complex (**21**)



Stretch:	12.7311
Bend:	67.0124
Stretch-Bend:	1.1172
Torsion:	-7.2672
Non-1,4 VDW:	0.2641
1,4 VDW:	36.4720
Charge/Charge:	50.6989
Charge/Dipole:	2.3108
Dipole/Dipole:	6.4014
Total:	169.7407