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A PROPELLER-SHAPED MESOMERIC BETAINE, TETRAPHENYLBENZENE-1-QUINOLINIUM-2-BENZOATE

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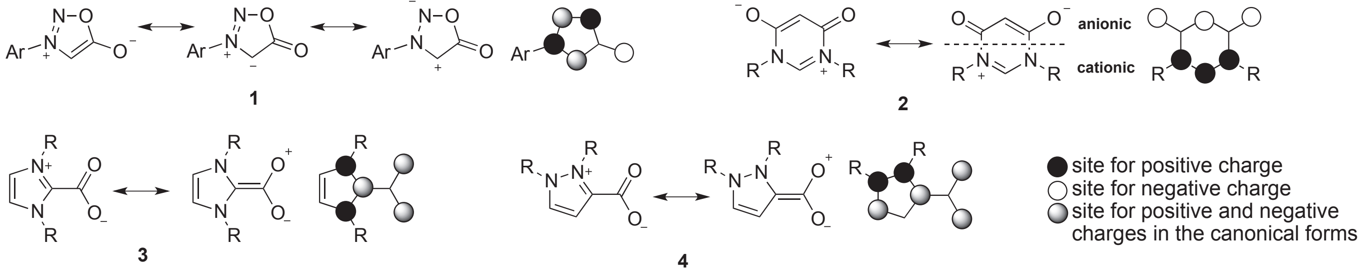
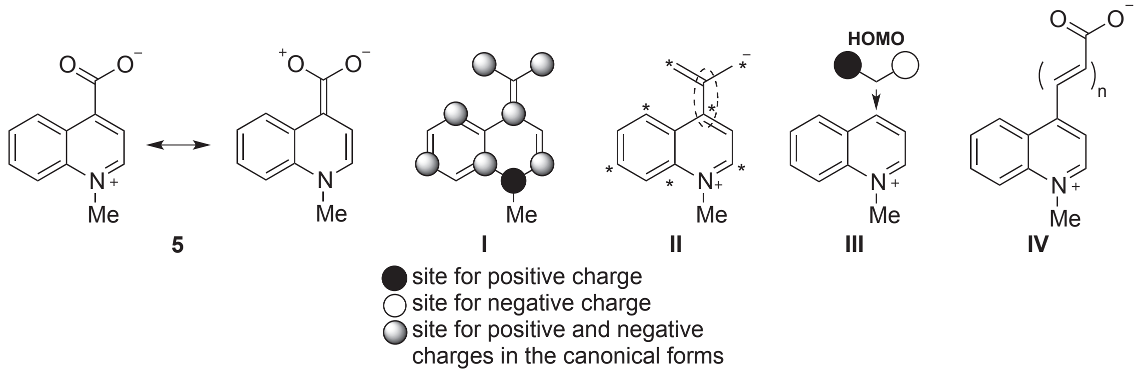
Abstract – 4-[(Quinolin-4-yl)ethynyl]benzoic acid underwent a cycloreaction with tetraphenylcyclopentadienone to give the hexa(hetero)arylbenzene-1-(quinolin-4-yl)-2-(4-benzoic acid)-3,4,5,6-tetraphenylbenzene which was N-methylated and finally deprotonated to give the title compound. The molecule adopts a propeller-shaped configuration in which the benzoate ring as well as the phenyl ring adjacent to the quinolinium substituent display non-isochronous resonance frequencies, respectively, due to a hindered rotation. Although the molecule formally belongs to the class of pseudo-cross-conjugated heterocyclic mesomeric betaines, the propeller-shape causes a charge distribution of cross-conjugated systems. DFT-calculations (frontier orbital profiles, geometries) have been carried out

Mesomeric betaines are conjugated molecules which can exclusively be represented by dipolar resonance forms which delocalize an equal number of positive and negative charges within a common π-conjugated system.[1] Their physical as well as chemical properties are governed by their type of conjugation.[1-5] According to a recent classification, conjugated, cross-conjugated, pseudo-cross-conjugated, semi-conjugated, and pseudo-semi-conjugated heterocyclic mesomeric betaines can be differentiated.[2-5] Sydnones **1** are well-known representatives of conjugated mesomeric betaines (CMB),[6,7] whereas 6-oxo-pyrimidinium-4-olates **2** are examples of cross-conjugated mesomeric betaines (CCMB). One of the main differences between these two classes of compounds is that CMBs possess common atoms for either charge in the resonance forms, whereas the charges of CCMB are strictly separated according to the rules of resonance (Scheme 1). Heteroarenium-carboxylates like imidazolium-2-carboxylates **3**,[8-10] pyrazolium-3-carboxylates **4**,[11] indazolium-3-carboxylates,[12,13] and pyridinium-2-carboxylates[14-17] are pseudo-cross-conjugated mesomeric betaines (PCCMB). Characteristically, common atoms for the delocalization of the negative as well as of the positive charges exist, if electron-sextet structures without external octet-stabilization are taken into account as shown.[1] Limited information is currently available about semi-conjugated and pseudo-semi-conjugated mesomeric betaines.[2-5]



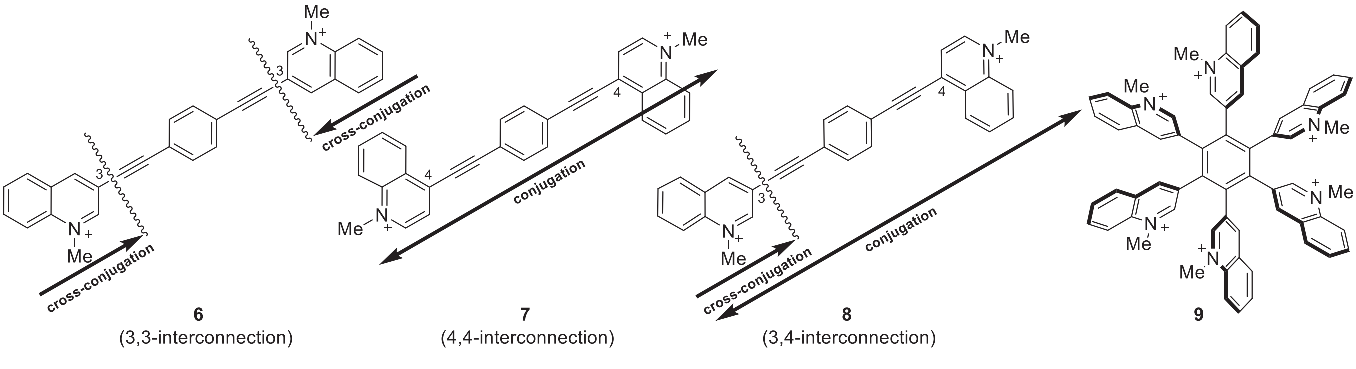
Scheme 1

Quinolinium-4-carboxylate **5** is an additional example of a PCCMB. Similar to **3** and **4**, common atoms for either charge exist in the canonical forms (**I**) (Scheme 2). Additional characteristics are as follows. According to Coulson, Rushbrooke, and Longuet-Higgins conjugated hydrocarbons can be classified as odd alternant, odd non-alternant, even alternant, and even non-alternant, and this classification was used for the classification of mesomeric betaines by Ollis, Stanforth, and Ramsden in 1985.[1] Thus, quinolinium-4-carboxylate **5** is isoconjugate with the odd alternant hydrocarbon **II**.[1] Its carboxylate group is isoconjugated with the propen-2-yl hydrocarbon fragment and, characteristically, this fragment is joined *via* an unstarred position to the cationic fragment of the molecule (**II**). This interconnection interrupts conjugation, because the unstarred position is the nodal position of the highest occupied molecular orbital HOMO (**III**).[18,19] It has therefore been concluded that the charges are effectively, but not exclusively delocalized in separated parts of the π-electronic system.[1] The classification translates well into the physical and chemical properties of mesomeric betaines. Thus, sydnones **1** as well as other conjugated mesomeric betaines are versatile 1,3-dipoles in heterocycle synthesis.[6,7] By contrast, cross-conjugated mesomeric betaines such as **2** undergo mainly 1,4-dipolar cycloadditions due to their π-electronic characteristics.[1] The pseudo-cross-conjugation of mesomeric betaines such as **3** and **4** translates into chemistry in such a way that they proved to be valuable starting materials for the *in-situ* generation of N-heterocyclic carbenes (NHC) by decarboxylation.[20,21] On the other hand, anionic N-heterocyclic carbenes can be generated from conjugated as well as cross-conjugated MBs by deprotonation.[21-23] The interesting area of overlap between the substance classes of N-heterocyclic carbenes and mesomeric betaines has been reviewed.[21] Structure **5** can be taken as model compound for a series of derivatives, because the insertion of double bonds and/or additional phenyl rings (**IV**) does not change the type of conjugation.[1]



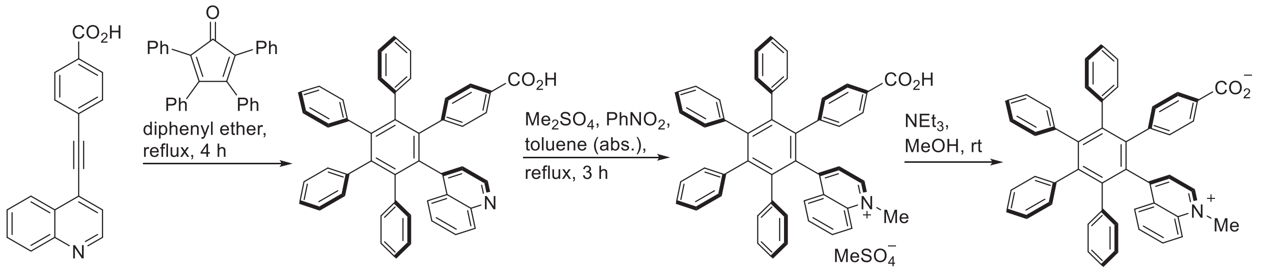
Scheme 2

In the course of our projects dealing with the types of conjugation[24,25] we studied systematically planar dicationic systems such as **6**, **7**, and **8** in which the positive charges are in conjugation, cross-conjugation, or a combination of both, and which have a considerable influence on their properties[26] (Scheme 3). Regardless of the interconnection, propeller-type polycations such as **9**, however, cannot be conjugated due to the torsion angle between quinolinium rings and the central core.[27,28] In continuation of these studies we report here on the synthesis and the properties of a propeller-shaped mesomeric betaine.



Scheme 3

The reaction of 4-(quinolin-4-ylethynyl)benzoic acid **10**[24] with cyclopentadienone in diphenyl ether gave the hexa(heteroaryl)benzene (HHAB) **11** in 80% yield as a yellow solid (Scheme 4). Methylation of **11** with dimethyl sulfate in the presence of catalytic amounts of nitrobenzene is almost quantitative and gave salt **12** in excellent yield. Deprotonation of **12**, which is insoluble in non-polar organic solvents such as chloroform, was accomplished by 1.3 equivalents of trimethylamine in methanol and gave the target betaine **13**, which proved to be very stable, in 88% yield. The deprotonation is accompanied by a color change from yellow to greenish. In contrast to its cationic precursor **12**, the mesomeric betaine **13** is a neutral compound and is soluble in chloroform. In comparison to **11**, two additional ^{13}C NMR signals were found on measuring **12**, which correspond to the carbon atoms of the N$^+$-CH$_3$ group and to the carbon of the counterion (45.1 and 52.8 ppm, respectively). On betaine formation, the signals of the anion disappeared.

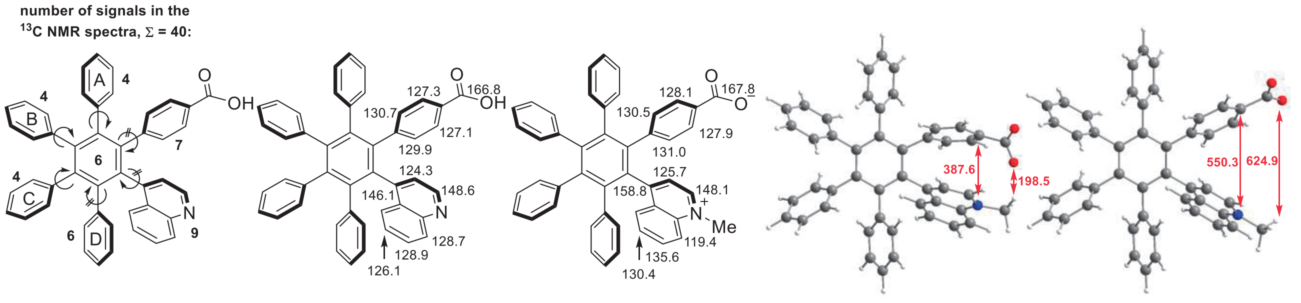


10 **11** (80%) **12** (96%) **13** (88%)

Scheme 4

Similar to hexaphenylbenzene which adopts a propeller conformation with torsion angles of 65° between the central core and the wings in the single crystal,[29-31] the six peripheral rings of **11** – **13** cannot lie in the plane of the central benzene ring. Whereas one set of signals in the ^{13}C NMR spectrum of hexaphenylbenzene and one overlapped signal with a center of gravity at 6.83 ppm (30H) in its proton resonance spectrum can be detected,[32] the ^{13}C NMR spectrum of HHAB **11** in DMSO-d_6 at 25 °C displayed 40 distinct signals of its 46 carbon atoms. By means of 2D NMR the identification of 18 signals of the *cis*-4-(2-(quinolin-4-yl)vinyl)benzoic acid fragment of **11** was possible. Eight additional signals belong to the eight quaternary carbon atoms which connect the phenyl rings **A**-**D** to the central benzene ring. The remaining 14 signals belong to the CH groups of the phenyl rings **A**-**D** some of which are isochronous due to rotation in solution. The four CH groups in *para*-positions of the phenyl rings **A-D** have to be assigned to four independent resonance frequencies as the molecule is non-symmetric. Due to hindered rotation, the *ortho* and *meta* carbon atoms of the benzoic acid fragment give four independent signals, and, in analogy to earlier results,[27] four additional resonance frequencies are caused by the non-isochronous *ortho* and *meta* CH groups of phenyl ring **D** adjacent to the quinolinium ring. The interaction with the quinolinium ring causes an upfield shift of the phenyl ring **D** in the NMR spectra in comparison to the rings **A-C**. In agreement to conclusions in the literature concerning hexaphenylbenzene[32] and own earlier results,[27] the six remaining ^{13}C signals have to be assigned to the twelve *ortho* and *meta* carbon atoms of the phenyl rings **A**-**C** which are isochronous due to rotation in solution. On conversion of **11** into the salt **12** and the betaine **13** the symmetry of the ring system is not changed. As an example, the *ortho* and *meta* positions of the benzoate moiety remain non-isochronous.

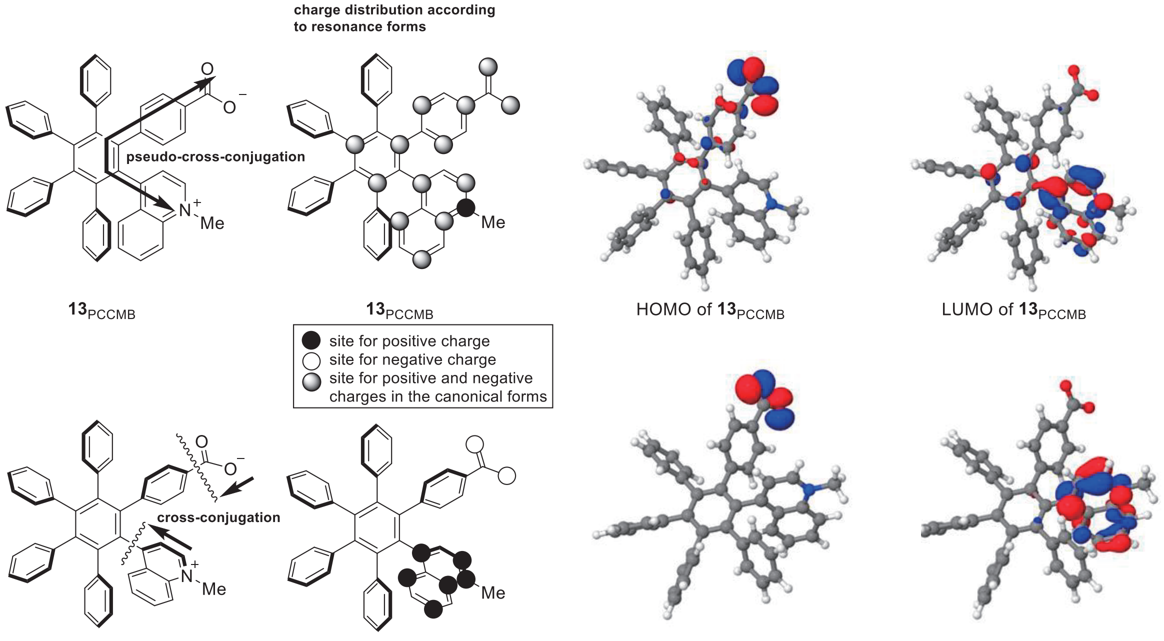
On betaine formation, the chemical shifts change as exemplified in Figure 1. Calculations of the true minimum structure of the target mesomeric betaine **13** were performed at the N31G6*/PBE0-D3 level. Due to the strong distortion of the vacuum structure of betaine **13** caused by the attracting charges, a DMSO solvent field was included in the calculation (Figure 1). The dihedral angles between all side wings and the central phenyl core of betaine **13** are in the range from 58° to 72° *in vacuo* and from 63° to 71° in DMSO, and the torsion angles between the quinolinium and the benzoate to the central core, respectively, are 67°/73° *in vacuo* and 71°/62° in DMSO according to the calculation.



11 **11** **13** **13** *in vacuo* **13** in DMSO

Figure 1. Selected NMR data and optimized structures *in vacuo* and DMSO according to a DFT calculation. Selected distances in pm.

The 2'-(quinolinium-4-yl)-1,1'-biphenyl-4-carboxylate fragment of **13** is a pseudo-cross-conjugated mesomeric betaine **13**$_{\mathrm{PCCMB}}$ in its planar form (Figure 2), as common atoms for either charge exist.



13$_{\mathrm{CCMB}}$ **13**$_{\mathrm{CCMB}}$ HOMO of 13$_{\mathrm{CCMB}}$ LUMO of 13$_{\mathrm{CCMB}}$

Figure 2. HOMO/LUMO profiles of the title betaine **13** in DMSO

Its propeller configuration, however, prevents conjugation so that the molecule *de facto* belongs to the class of cross-conjugated mesomeric betaines **13**$_{\mathrm{CCMB}}$. As a consequence, the charges are restricted to separated parts of the common π-electron system according to the resonance forms. The frontier orbital profiles confirm the proposed charge distributions in either form. We calculated the highest occupied (HOMO) and lowest unoccupied molecular orbital (LUMO) of **13**$_{\mathrm{PCCMB}}$ by setting the torsion angles around the benzoate-phenyl and quinolinium-phenyl bonds to 0°, respectively.

The highest occupied molecular orbital (HOMO) is located on the carboxylic group, whereas the lowest unoccupied molecular orbital (LUMO) is located in the quinolinium ring in accordance with its classification as cross-conjugated mesomeric betaine in its twisted form. The partially planar configuration of **13** is by 161.53 kJ/mol more instable than the twisted one due to strong steric hindrance in the planar configuration. The band gaps between HOMO and LUMO are smaller in the planar form and were calculated to be -3.1783 and -3.3116 eV in the flattened and twisted form, respectively. Due to the propeller configuration, the benzoate group does not influence the electronic spectra of the betaine. Benzoic acid is known to have its low-lying excitation at 272 nm which shifts to 259 nm on deprotonation, and substituents in the range between the Hammett´s constants of σ = -0.66 (NH_2) and +0.15 (SH) cause shift changes between $\Delta\lambda$ = 14 nm and 6 nm.[33] The HHAB **11** and its non-carboxylated derivative,[27] however, show almost identical UV/Vis absorption spectra with main asymmetric peaks at 214 / 213 nm and small absorptions at 316 / 317.5 nm. The salt **12** and its non-carboxylated derivative absorb at 214 / 215.5, 240.5 / 240.7 and 319 / 320 nm. The UV/VIS spectrum of the mesomeric betaine **13** shows absorptions at 215, 240.5, and 320 nm so that the carboxylate group just plays the role of a substituent without remarkable influence on the π-electronic system of the molecule.

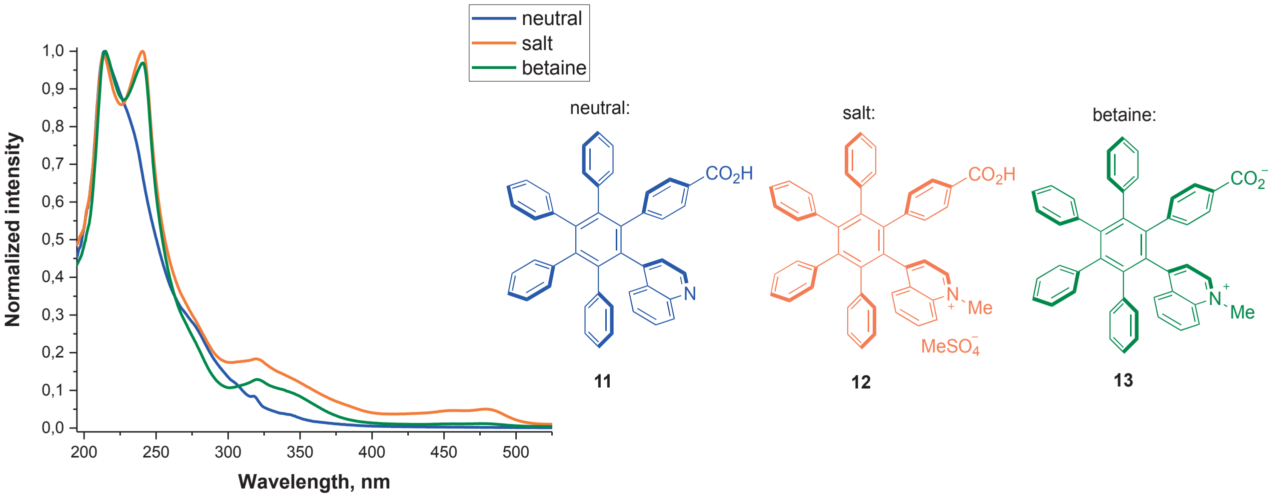


Figure 3. UV spectra

The type of conjugation of mesomeric betaines can be governed by torsion angles. The propeller-shaped title mesomeric betaine **13** delocalizes its charges in separated parts of the π-electronic system due to the torsion angles of 58 – 72° between the charged fragments, *i.e.* quinolinium and benzoate. Thus it is *de facto* a cross-conjugated mesomeric betaine. Diminished torsion angles, which are energetically strongly disfavored according to DFT calculations, caused a different charge-distribution throughout the molecule which changes the type of conjugation to pseudo-cross-conjugation, to which the title betaine formally belongs.

EXPERIMENTAL

General considerations. All chemicals were purchased and used without further purification unless otherwise mentioned. Anhydrous solvents were dried according to standard procedures before usage. Melting points are uncorrected and were determined in an apparatus according to Dr. Tottoli (Büchi). The ATR-IR spectra were obtained on a Bruker Alpha in the range of 400 to 4000 cm^{-1}. ^{1}H NMR spectra were recorded at 600 MHz. ^{13}C NMR spectra were recorded at 150 MHz, with the solvent peak used as the internal reference. Multiplicities are described by using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet. Signal orientations in DEPT experiments were described as follows: o = no signal; + = up (CH, CH_3); - = down (CH_2). The HRMS spectra were obtained with a Bruker Impact II, a Bruker Daltonik Tesla-Fourier transform-ion cyclotron resonance mass spectrometer, or with a Waters Micromass LCT with the direct inlet.

Calculations. All density-functional theory (DFT)-calculations were carried out by using the multithreaded Firefly 8.2.0 QC package,[34] which is partially based on the GAMESS (US)[35] source code, running on Windows 10 Pro (Version 10.0.17763.475) (x86_64) on a 16 core AMD 2950X processor workstation. MM2 optimized structures were used as starting geometries. Complete geometry optimizations were carried out on the implemented N31G6* basis set and with the PBE0 density functional including D3 dispersion correction. All calculated structures were proven to be true minima by the absence of imaginary frequencies. Solvent effects in DMSO were estimated by help of the polarizable continuum model implemented in Firefly. Orbital plots were obtained using Jmol 14.27.2.[36]

1-(Quinolin-4-yl)-2-(4-benzoic acid)-3,4,5,6-tetraphenylbenzene 11.

Diphenyl ether (10 g) was melted in 50 mL round-bottomed flask fitted with an air condenser. 4-[(Quinolin-4-yl)ethynyl]benzoic acid **10**[24] (0.137 g, 0.50 mmol) and tetraphenylcyclopentadienone (0.240 g, 0.62 mmol) were added to the flask, which was heated for 4 h using a heat gun. The solution was then cooled to rt. After cooling, *n*-hexane (50 mL) was added, resulting in the precipitation of a gray powder, which was collected by vacuum filtration, and dissolved in EtOAc (3 × 20 mL). The solvent was then removed and the product was dried under vacuum. The product was obtained as a yellow solid. Yield: 0.252 g (80%). Mp >330 °C (decomp.). **^{1}H NMR** (600 MHz, DMSO-d_6): δ = 12.81 (br s, 1H, COO*H*), 8.48 (d, *J* = 4.4 Hz, 1H, 2-H), 7.81 (d, *J* = 8.2 Hz, 1H, 5-H), 7.68 (d, *J* = 8.3 Hz, 1H, 8-H), 7.55 (ddd, *J* = 1.4, 6.9, 8.3 Hz, 1H, 7-H), 7.51 (ddd, *J* = 1.3, 6.9, 8.2 Hz, 1H, 6-H), 7.34 (dd, *J* = 1.7, 8.1 Hz, 1H, 3′-H), 7.31 (d, *J* = 4.4 Hz, 1H, 3-H), 7.14 (dd, *J* = 1.6, 8.1 Hz, 1H, 2′-H), 7.06 (dd, *J* = 1.7, 8.1 Hz, 1H, 5′-H), 7.02-6.98 (m, 4-H, Ph), 6.92-6.80 (m, 14H, Ph), 6.80 (dd, *J* = 1.6, 8.1 Hz, 1H, 6′-H), 6.68-6,65 (m, 2H, Ph), 6.54-6.52 (m, 1H, Ph) ppm. **^{13}C NMR** (150 MHz, DMSO-d_6): δ = 166.8 (o, *C*OO), 148.6 (+, C2), 146.9 (o, C8a), 146.1 (o, C4), 144.1 (o, C1′), 141.0 (o), 140.6 (o), 140.1 (o), 139.9 (o), 139.6 (o), 139.5 (o), 139.3 (o), 139.08 (o), 139.12 (o, Cβ), 135.0 (o, Cα), 132.1 (+), 131.0 (+), 131.0 (+), 130.9 (+), 130.7 (+, C2′), 130.64 (+), 130.61 (+), 129.9 (+, C6′), 129.7 (+), 129.5 (+), 128.9 (+, C7), 128.7 (+, C8), 127.9 (o, C4′), 127.3 (+, C3′), 127.1 (+, C5′), 126.9 (o, C4a), 126.73 (+), 126.68 (+), 126.64 (+), 126.59 (+, C5), 126.1 (+, C6), 125.8 (+), 125.7 (+), 125.6 (+), 124.3 (+, C3) ppm. **IR (ATR)** $\tilde{\nu}$ = 3055, 3025, 2920, 1791, 1695, 1602, 1586, 1506, 1496, 1442, 1403, 1372, 1236, 1215, 1173, 1100, 1072, 1042, 1017, 851, 813, 761, 696, 566, 553, 546, 502 cm^{-1}. **HRMS (APCI):** [$C_{46}H_{32}NO_2^{+}$] required: 630.2428. Found 630.2429.

1-(1-Methylquinolinium-4-yl)-2-(4-benzoic acid)-3,4,5,6-tetraphenylbenzene methylsulfate 12.

The reaction was carried out under an atmosphere of nitrogen. A solution of 0.100 g (0.160 mmol) of 1-(quinolin-4-yl)-2-(4-benzoic acid)-3,4,5,6-tetraphenylbenzene **11**, 0.05 mL of nitrobenzene and 0.06 mL (0.63 mmol) of dimethyl sulfate in 5 mL of anhydrous toluene was heated (3 h) under reflux temperature. After completion of the reaction (controlled by TLC), the solution was cooled, the crude product was filtered off, washed with EtOAc (3 × 10 mL), and dried to afford 1-(1-methylquinolinium-4-yl)-2-(4-benzoic acid)-3,4,5,6-tetraphenylbenzene methylsulfate **12**. The product was obtained as a yellow solid. Yield: 0.115 (96%). Mp 204 °C (decomp.). **^{1}H NMR** (600 MHz, DMSO-d_6): δ = 9.15 (d, *J* = 6.1 Hz, 1H, 2-H), 8.27 (d, *J* = 8.5 Hz, 1H, 5-H), 8.21 (d, *J* = 8.8 Hz, 1H, 8-H), 8.15 (d, *J* = 6.1 Hz, 1H, 3-H), 8.12 (ddd, *J* = 1.2, 7.3, 8.6 Hz, 1H, 7-H), 7.96 (t, *J* = 7.5 Hz, 1H, 6-H), 7.42 (dd, *J* = 1.6, 8.1 Hz, 1H, 3′-H), 7.21 (dd, *J* = 1.4, 8.1 Hz, 1H, 2′-H), 7.14 (dd, *J* = 1.6, 8.1 Hz, 1H, 5′-H), 7.06 (d, *J* = 7.9 Hz, 1H, Ph), 7.04-7.00 (m, 3H, Ph), 6.96-6.82 (m, 14H, 6′-H, Ph), 6.75-6.72 (m, 1H, Ph), 6.71-6.70 (m, 1H, Ph), 6.59 (t, *J* = 7.6 Hz, 1H, Ph) 4.41 (s, 3H, NCH_3), 3.37 (s, 3H, CH_3SO$_4$) ppm. **^{13}C NMR** (150 MHz, DMSO-d_6): δ = 166.7 (o, *C*OO), 157.9 (o, C4), 147.7 (+, C2), 143.1 (o, C1′), 142.4 (o), 141.0 (o), 139.5 (o), 139.2 (o), 138.9 (o), 138.7 (o), 138.5 (o, Cβ), 138.1 (o), 137.2 (o, C8a), 135.2 (+, C7), 132.7 (o, Cα), 130.98 (+), 130.95 (+), 130.8 (+, C2′), 130.51 (+), 130.48 (+), 130.1 (+, C6′), 130.0 (+), 129.8 (+, C6), 129.2 (+, C5), 128.9 (o), 128.5 (o, C4′), 128.18 (o, C4a), 127.9 (+, C3′), 127.6 (+, C5′), 126.90 (+), 126.88 (+), 126.85 (+), 126.83 (+), 126.75 (+), 126.72 (+), 126.5 (+), 126.0 (+), 126.9 (+), 125.2 (+, C3), 118.9 (+, C8), 52.8 (+, CH_3SO_4), 45.1 (+, NCH_3) ppm. **IR (ATR)** $\tilde{\nu}$ = 3055, 2943, 1733, 1706, 1604, 1583, 1529, 1497, 1442, 1371, 1240, 1200, 1176, 1116, 1045, 1006, 911, 865, 817, 725, 698, 669, 609, 577, 556, 434 cm^{-1}. **HRMS (ESI):** [$C_{47}H_{34}NO_2^+$] required: 644.2585. Found 644.2585.

1-(1-Methylquinolinium-4-yl)-2-(4-benzoate)-3,4,5,6-tetraphenylbenzene 13.

To a solution of 0.100 g (0.13 mmol) of 1-(1-methylquinolinium-4-yl)-2-(4-benzoic acid)-3,4,5,6-tetraphenylbenzene methylsulfate **12** in MeOH (4 mL) was added 0.021 mL (0.15 mmol) of NEt_3. The resulting mixture was evaporated, the crude product washed with water, and dried *in vacuo* to give 1-(1-methylquinolinium-4-yl)-2-(4-benzoate)-3,4,5,6-tetraphenylbenzene **13**. The product was obtained as a greenish solid: Yield: 0.073 g (88%). Mp 287 °C (decomp.). **^{1}H NMR** (600 MHz, DMSO-d_6): δ = 9.15 (d, J = 6.0 Hz, 1H, 2-H), 8.26 (dd, J = 0.9, 8.8 Hz, 1H, 5-H), 8.18 (d, J = 8.5 Hz, 1H, 8-H), 8.13 (d, J = 6.0 Hz, 1H, 3-H), 8.10 (ddd, J = 1.2, 7.2, 8.4 Hz, 1H, 7-H), 7.96 (t, J = 7.7 Hz, 1H, 6-H), 7.33 (dd, J = 1.4, 8.0 Hz, 1H, 5′-H), 7.06-7.04 (m, 3H, 3′-H, 6′-H, Ph), 7.01-7.00 (m, 3H, Ph), 6.95-6.82 (m, 15H, Ph), 6.85 (m, 2′-H), 6.73 (d, J = 7.44 Hz, 1H, Ph), 6.71-6.69 (m, 2H, Ph), 6.58 (t, J = 7.6 Hz, 1H, Ph) ppm. **^{13}C NMR** (150 MHz, DMSO-d_6): δ = 167.8 (o, COO), 158.8 (o, C4), 148.1 (+, C2), 142.8 (o), 141.2 (o), 141.0 (o, C1′), 139.9 (o), 139.8 (o), 139.7 (o), 139.4 (o), 139.3 (o), 138.7 (o, Cβ), 137.6 (o, C8a), 135.6 (+, C7), 133.4 (o, Cα), 131.5 (+), 131.3 (+), 131.0 (+, C6′ plus 2 more signals, overlapped), 130.5 (+, C2′), 130.4 (+, C6), 129.8 (+, C5), 128.7 (o, C4a), 128.1 (o, C3′), 127.9 (+, C5′), 127.29 (+), 127.27 (+), 127.25 (+), 127.24 (+), 127.22 (+), 127.20 (+), 127.15 (+), 126.9 (+), 126.4 (+), 126.29 (+), 126.27 (+), 125.7 (+, C3), 119.4 (+, C8), 45.6 (+, NCH_3) ppm. **IR (ATR)** $\tilde{\nu}$ = 3053, 3026, 1713, 1601, 1527, 1496, 1441, 1368, 1227, 1173, 1016, 763, 727, 696, 554 cm^{-1}. **HRMS (ESI):** [$C_{47}H_{34}NO_2^+$] required 644.2585. Found 644.2581. [$C_{47}H_{33}NNaO_2^+$] required 666.2404. Found 666.2399.

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