Synthesis and characterization of propeller-shaped mono- to hexacationic quinolinium-substituted benzenes†

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Diels–Alder reaction of 2-, 3- and 4-((phenylethynyl)quinolines and tetraphenylcyclpentadienone gave three regioisomeric 2,3,4,5,6-pentaphenyl-1-(quinolin-2-yl)-3-y1, and 4-y1-benzenes. Restricted rotation of the 3-y1 and 4-y1 substituted derivatives is observed between the central core and the substituents, resulting in propeller-shaped molecules. Likewise, 1,2-diquinolinyl-3,4,5,6-tetraphenylbenzenes with 3-y1,3-y1 and 3-y1,4-y1 connectivity were prepared. As evidenced by NMR spectroscopy, they form two diastereomers due to their restricted rotation. A cobalt-catalyzed [2 + 2 + 2]-cyclotrimerization of 2-(phenylethynyl)quinoline resulted in the formation of triphenyl-2,4,6- and 3,5,6-tri(quinolin-2-yl)benzenes. The same reaction was applied to 3,3-ethyne-1,2-diylquinoline which formed hexa(quinolin-3-yl)benzene. N-Methylation gave the title compounds. Among those, the hexacationic hexa(N-methylquinolinio-3-yl)benzene is described. Stereochemical aspects are predominantly discussed by means of results of NMR experiments. DFT-calculations on the most stable conformations and the frontier orbital profiles of the hexacation as well as of its neutral precursor have been carried out.

Introduction

Considerable attention has been directed toward heterocycle polycations as they are interesting in natural product chemistry, heterocyclic chemistry, and materials chemistry. Thus, polypyridinium alkaldoids (halotoxin, cyclostellettamin C, amphitoxin, viscosamine, viscosaline, pachychalines A–C) are polycationic molecules from nature. Streitwieser et al. reported on series of polypyridinium salts and betaines which have adjacent heteroaromatic rings in conjugation. Thus, the five-fold pyridinium substituted cyclopentadiene anion possesses structure elements of conjugated mesomeric betaines. The SASAPOS protocol (self-activated silyl-assisted polyenio substitution) by Weiss et al. allowed for the synthesis of a variety of heteroaromatic substituted substrates, for which 2 is given as an example here. This widely applicable protocol takes advantage of the fact that a substrate which bonds neutral ligands such as chloride undergoes a substitution with heteroaromatic nucleophiles equivalent to the quantity of the bonding ligands in the presence of the same number of equivalents of trimethylsilyltriflate (TMSOTf). We reported on heterocycle polycations with heteroaromatic central cores such as pyridine, pyrimidine, pyrazine, pyridazine, 1,3,5-triazine, and purine. An example is pentacationic pyridine polycations proved to be versatile starting materials for the synthesis of highly substituted pyridines with various substitution patterns. Apart from their synthetic applicabilities, heterocycle polycations are of interest as potential semiconductors, photosensitive materials, oxidants, and biologically active compounds like herbicides, acetylenic substrates, and cholinesterase inhibitors. A recent review article summarizes results achieved so far (Scheme 1).

Steric hindrance exerted by the peripheral ligands cause propeller-shaped molecules. Recently, the sterically congested hexa(heteroaryl)benzene (HHAB) was formed as two isolable isomers which differ only in the rotation of one methyl-pyridine group. In general, propeller-shaped hexaarylbenzenes (HABs) such as hexa(naphthyl)benzene have numerous applications in materials sciences as they play roles as liquid crystals, microporous organic solids, molecular capsules, supramolecular electronic materials, molecular rotors, nonlinear optical materials, metal sensors, redox materials, and molecular wires. We report here on quinolinium-substituted benzenes which combine the features of HHABs and polycations as they have to adopt propeller-shaped...
configurations due to the additional benzo-annulation in comparison to their pyridinium derivatives.

Results and discussion

First, Sonogashira–Hagihara coupling reactions were used to prepare three isomeric ethynyl-substituted quinolines as starting materials for the synthesis of monoquinolinyl-substituted pentaphenylbenzenes, which are of potential interest as ligands of organic electroluminescent device materials. 33 Thus, the 2-, 3-, and 4-halosubstituted quinolines 6a–c and phenylacetylene 7 were reacted to give the quinolines 8a–c in good yields (Scheme 2). With these compounds in hand, we examined the [4 + 2]-cycloaddition with tetraphenyliclopentandione 9. The reaction did not proceed under a variety of different conditions that were tested, among those reflux temperature in benzene, toluene, and xylene, respectively. On increasing the reaction temperature to 305 °C by using benzophenone as a solvent, however, the quinolines 10a–c were finally prepared within 30 min in moderate yields.

Similar to hexaphenylbenzene, the six peripheral rings of 10a–c cannot lie in the plane of the central benzene ring. Whereas in solution, on the NMR time scale, the peripheral rings are perpendicular to the plane of the central ring in the absence of appropriate substitutions, the X-ray structure of hexaphenylbenzene itself showed a propeller conformation with angles around the Ph–Ph bonds of approximately 65°. 34 It is known that methyl and methoxy groups in C₆Ar₆ systems in ortho position cause a barrier of rotation of approximately 33 kcal mol⁻¹, whereas this value is considerably decreased to approximately 17 kcal mol⁻¹ for the case of meta-substitutions. 23 Hexaphenylbenzene C₆Ph₆ consequently displays one set of signals in the ¹³C NMR spectra and one overlapped signal with a center of gravity at 6.83 ppm (30H) in the proton resonance spectra. 35 The chemical shifts of 10a–c are different as a consequence of their isomerism and, in addition, intermolecular interactions (Fig. 1). The broadening of the signals at approximately 7.00 ppm in the spectrum of 10a (blue) can be attributed to N⋯H–C interactions to the nitrogen atom, which is not possible in 10b,c. These interactions are thought to be within the limits of hydrogen bonds and classical van der Waals contacts. 36 The upfield shift of phenyl ring signals due to intramolecular π-interactions caused by the quinolin-4-yl substitution of 10c can clearly be seen (black), which are less in 10a,b.

The steric hindrance of the quinoline rings can be compared with 1-(3,4-dimethylphenyl)-2,3,4,5,6-pentaphenylbenzene 37 for 10a,b and 1-(2,3-dimethylphenyl)-2,3,4,5,6-pentaphenylbenzene, which seems to be unknown, for 10c.

![Scheme 1](image1.png)

**Scheme 1** Examples of heterocycle polycations and of propeller-shaped molecules.

![Scheme 2](image2.png)

**Scheme 2** Synthesis of monoquinoline-substituted HHABs.

![Fig. 1](image3.png)

**Fig. 1** Comparison of ¹H NMR spectra of HHABs 10a (1), 10b (2), and 10c (3) (DMSO-d₆, 25 °C).
However, the quinolin-4-yl-substitution pattern of $10c$ imitates the steric hindrance of the methyl group in the model compound 1-(2-methylphenyl)-2,3,4,5,6-pentaphenylbenzene which has a propeller-type topology in the solid and a slow rotation of the o-tolyl group at 25 °C in solution. For the case of free rotation under the measurement conditions, 25 distinct $^{13}$C NMR resonance frequencies can be expected for $10a$–$c$, among those 15 signals of CH groups. For the case of restricted rotation, this number is increased to 29 $^{13}$C NMR signals in total, and 19 signals of CH groups, because the ortho- and meta-positions of the 2- and 3-phenyl substituents become non-isochronous. The least sterically hindered compound $10a$ displays 22 distinct signals due to overlapping in DMSO-$d_6$ at 25 °C. Compound $10b$ shows the expected 29 signals for a restricted rotation, and $10c$ displays in total 27 distinct resonance frequencies under the same measurement conditions, presumably due to overlapping of two signals.

The same protocol was applied to the reaction of quinoline $14$ with two alkynyl residues which was prepared in 21% yield in three steps from 1,4-dibromobenzene $11$ via $12$ and $13$ as shown (Scheme 3). Quinoline $14$ reacted with an excess of cyclopentadienone $9$ to give compound $15$ which precipitated as exclusive reaction product during the work-up procedure in good yield.

The method is also applicable to prepare isomeric diquinolinyl substituted tetraphenylbenzenes (Scheme 4). Thus, under analogous conditions, the compound $19a$ with quinolin-3-yl/3-yl connectivity and the isomeric quinolin-3-yl/4-yl derivative $19b$ were prepared in 90% and 78% yield, respectively, starting from $18a,b$ which are available starting from $6b,c$ and $17$ by standard procedures. The quinolin-3-yl,3-yl compound $19a$ can exist in two diastereomeric forms due to restricted rotation, a $C_s$ conformation and a racemic pair with $C_2$ symmetry, similar to hexaarylbenzenes with two meta-substituents at 0 °C on the NMR time scale. The $^1H$ NMR spectrum of $19a$ showed 37 of expectable $48$ $^{13}$C NMR signals. Two sets of partially overlapped signals can be identified in a ratio of 1 : 0.8 under the measuring conditions (DMSO-$d_6$, 25 °C). The 4-H hydrogen atom of the quinoline residues of one isomer appears at 7.97 ppm, whereas the other is detectable at 7.93 ppm. The $^{13}$C NMR spectrum of isomer $19b$, which possesses a quinolin-3-yl,4-yl connectivity, shows 72 distinct signals of expectable 96. This number is due to the fact, that the 3-yl,4-yl connectivity causes an additional non-symmetry of the molecule and consequently non-isochronous substituents of the two magnetically inequivalent isomers. Under the same measuring conditions, two isochronous rotameric forms are present in a ratio of 1 : 1 in the NMR spectrum of $19b$.

For the synthesis of HHABs with three quinoline residues another approach was applied. Thus, the asymmetric acetylene $8a$ was subjected to a cobalt-catalyzed [2 + 2 + 2]-trimerization reaction which has already been applied for the synthesis of HABs before (Scheme 5). The trimerization of $8a$ gave a mixture of two separable regioisomers $20a$ and $20b$ (1 : 3) with a total yield of 40%. Compound $20a$ is a heteroaromatic analogue of 1,3,5-tri(α-naphthyl)-benzene, a propeller-like, non-planar molecule that is known to interlock in the melt. It displays 15 $^{13}$C NMR signals, similar to the corresponding number of signals of $D_{3h}$ symmetric oligophenylenes which were expected within the fast exchange limit for all single bond rotations.

Similar to the spectra of the mono(quinolin-2-yl)derivative $10a$, the signals of the ortho- and meta-protons
appear as broad singlets due to N-H-C interactions. Assignment of all atoms using 2D spectra was possible; one set of proton signals for all three quinoline residues of 20a was found. It is known that ortho-substitutions, which cannot be taken as a model for the quinolin-2-yl substitution, can prevent rapid interconversion of the $C_{2v}$ and $C_{s}$ isomeric forms which are the result of the formation of syn- and anti-conformations. The 1,2,4-substituted compound 20b displays 36 of expectable 45 distinct $^{13}$C NMR resonance frequencies in DMSO-$d_6$ at 25 °C, if free rotation under the measurement conditions is presumed. Similar to compound 10a, a considerable broadening of the $^1$H NMR signals of the quinolines in DMSO-$d_6$ at 25 °C as well as the phenyl rings is observable.

Trimerization of the acetylene 18a was tested to prepare a hexaquinolin-3-yl substituted benzene. Indeed, HHAB 21 was formed in 83% yield (Scheme 6). Unfortunately, due to the rather limited solubility of 21 NMR analyses were not possible. Nonetheless, the corresponding HRMS ($m/z$ = 863.2896) in accord with the structure of 21 which can exist in eight rotameric forms. Literature-known calculated minimized energies of hexa($\beta$-naphthyl)benzene, the non-heteroaromatic analogue of 21, revealed that the most stable rotamer is the one in which all $\beta$-naphthyl residues are twisted onto the same side (6,0). The X-ray crystal analysis of hexa(2-pyridyl)benzene, however, revealed the $\alpha,\beta,\alpha,\beta,\alpha,\beta$ arrangement of pyridine rings and dihedral angles between the pyridyl substituent and the benzene ring of approximately 90°.

**Synthesis of polycationic HABs**

Based on former experiences of our group, dimethyl sulfate was used as a methylation agent to convert the quinoline derivatives into cationic species. First, the monoquinoline substituted HABs 10a-c were successfully methylated in anhydrous toluene under reflux conditions (Scheme 7). The N-methyl group of 22a interlocks the molecule and 19 distinct $^{13}$C NMR signals of CH groups are spectrally detectable plus the signals of the anion and the methyl group at 52.8 and 42.5 ppm, respectively. Thus, in contrast to 10a-c, 22a-c all display the same number of signals. The N-methyquinolinium salts of 15 with methylsulfate (23) and hexafluorophosphphate anions (23PF$_6$) were prepared as well, and the diquinoline HABs 19a,b were also successfully methylated. An immediate anion exchange reaction during work-up yielded the dihexafluoro-

**Scheme 6** Cobalt-catalyzed [2 + 2 + 2]-cyclotrimerization of 18a.

**Scheme 7** Methylation of quinoline-based HHABs.

phosphate salts 24a,b. Similar to the non-methylated precursors 19a and 19b, the number of $^{13}$C NMR resonance frequencies of 24a and 24b is 38 and 72, respectively. The 3-yl,3-yl salt 24a has an almost identical ratio of rotamers (1:0.9) as its non-methylated precursor, and the corresponding ratio of the salt 24b in DMSO-$d_6$ is 1:1.27. In summary, except for 10a, no spectroscopically detectable changes of the symmetry of the molecules is caused by the methylations. On methylation, the UV/Vis absorption maxima display bathochromic shifts. The spectra are shown in the ESL.†

Finally, N-methylation of 21 with an excess of dimethyl sulfate followed by precipitation with NH$_4$PF$_6$ successfully gave the fully methylated hexacationic HHAB 25 (Scheme 8) which is soluble in DMSO-$d_6$ and which could be characterized completely.

Theoretically, the salt 25 can exist in eight rotameric forms A-H. Similar to hexa($\beta$-naphthyl)benzene, solving the simple combinatoric problem created by propeller-like compounds such as 21 or 25 results in the following ratio: A:B:C:D:E:F:G:H = 1:6:3:6:6:3:6:1. Fig. 2 shows
possible interconversions between the forms A–H, which we calculated in form of the hexactionic species (DFT, 6-31G*/PBE0). Schematically, the rotamers can be classified as those in which N-methylquinolinium residues are 6:0 (all-syn), 5-up/1-down, 4 up/2-down (1,2; 1,3; 1,4), and 3-up/3-down (1,2,3,1,2,4; 1,3,5) (Fig. 2). The calculated energy differences between the eight rotamers of 25 are extremely small, and so are the differences between the rotamers of 21. The lowest energy rotamer of 25 is the 3-up/3-down (1,3,5) isomer, whereas the all-syn isomer (6,0) has an energy of 7.65 kJ mol\(^{-1}\) and is thus the less stable. Similarly, the (6,0) rotamer of the neutral precursor 21 is by only 3.8 kJ mol\(^{-1}\) less stable than the (3,3)-1,3,5 rotamer. As a matter of fact, the rotamers of 25 cause signal overlaps in the \(^{1}H\) NMR spectrum at ambient temperature (Fig. 1, spectrum 1, ESI†). The spectra change reversibly on heating of the NMR sample successively from rt to 100 °C (Fig. 1, spectra 2–9); on cooling, the original spectrum is reconstituted (Fig. 1, spectrum 10). Obviously, no other ratio of sets of isochronous rotamers is formed during this temperature experiment. Calculations of all true minimum structures of 25 show that in all rotamers the dihedral angles between the quinoline and the phenyl rings are in the range from 71° to 88°.

Fig. 3 shows the calculated most stable conformer of 25 (calculated) (above). HOMO (left) and LUMO (right) of 25 (3,3)-1,3,5.

Conclusions

Series of propeller-shaped quinolinium-substituted benzenes as well as their electrostatically neutral precursors have been prepared under variation of the substitution site of the quinoline ring (2-yl, 3-yl, 4-yl), covering the range from the monocationic quinolinium-2,3,4,5,6-pentaphenylbenzene to the hexactionic hexakis(1-methylquinolinium-3-yl)benzene. The latter can exist in eight different rotamers, the (3,3)-1,3,5-isomer of which was calculated to be the most stable one. Due to the propeller-shape geometry which suppresses conjugation throughout the entire π-electron system, the frontier orbitals are located in the individual quinolinium rings.

Experimental

All reactions were carried out under an atmosphere of nitrogen in flame or oven-dried glassware. 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. Spectroscopic atom numberings are shown in the ESI.† Signal orientations in DEPT experiments were described as follows: o = no signal; + = up (CH, CH\(_3\)); − = down (CH\(_2\)).
The mass spectra (ESIMS) were measured with a Varian 320 MS Triple Quad GC/MS/MS (EIMS) or with an Agilent LCMSD series HP 1100 with APIES at fragmentor voltages as indicated. Samples were sprayed from MeOH at 4000 V capillary voltage and fragmentor voltages of 30 V unless otherwise noted. 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. Chromatography: The reactions were traced by thin layer chromatography with silica gel 60 (F254, company MERCK KGAA). For the detection of substances, quenching was used at either 254 nm or 366 nm with a mercury lamp. The preparative column chromatography was conducted through silica gel 60 (230–400 mesh) of the company MERCK KGAA. Yields are not optimized.

Calculations

All density-functional theory (DFT)-calculations were carried out by using the Firefly 8.2.0 QC package,48 which is partially based on the GAMESS (US) source code,49 running on Linux. All density-functional theory (DFT)-calculations were carried out by using the Firefly 8.2.0 QC package,48 which is partially based on the GAMESS (US) source code,49 running on Linux (72 processor workstations (Beowulf-cluster) with Infiniband interconnect and parallelized with MPICH 1.2.7p1). MM2 optimized structures were used as starting geometries. Complete geometry optimizations were carried out on the implemented 6-31G* basis set and with the PBE0 density functional. All calculated structures were proven to be true minima by the absence of imaginary frequencies. Partial charges were obtained with Jmol 14.27.2.

Synthesis

General procedure of Sonogashira–Hagihara coupling (Procedure 1)

The reactions were carried out under a nitrogen atmosphere. A mixture of 5 mmol of corresponding haloquinoline 1, 1 mol% of Pd(PPh3)2Cl2, and 2 mol% of CuI was suspended in 7 mL of dry NEt3 with stirring. A sample of the corresponding ethynylbenzene 2 (1.05 equiv.) in dry NEt3 was added dropwise at room temperature. Finally, a purification by column chromatography (petroleum ether:ethyl acetate = 5 : 1) gave 2-(phenylethynyl)quinoline 6a. The preparative column chromatography was conducted through silica gel 60 (230–400 mesh) of the company MERCK KGAA. Yields are not optimized.

3-(Phenylethynyl)quinoline (8b). According to Procedure 1, a solution of 2.080 g (10.00 mmol) of 3-bromoquinoline 6b, 0.070 g (0.10 mmol) of Pd(PPh3)2Cl2, 0.038 g (0.20 mmol) CuI and 1.071 g (10.50 mmol) of ethynylbenzene 7 in 30 mL of anhydrous NEt3 was heated over the period of 1.5 h under reflux temperature. Finally, a purification by column chromatography (petroleum ether:ethyl acetate = 3 : 1) gave 3-(phenylethynyl)quinoline 8b. Yield 2.290 g, 100%, a white solid, m.p. 83 °C.1H NMR (600 MHz, CDCl3); δ = 9.00 (d, J = 2.0 Hz, 1H, 2-H), 8.30 (d, J = 2.0 Hz, 1H, 4-H). 13C NMR (150 MHz, CDCl3); δ = 152.1 (+, C2), 146.8 (o, C8a), 138.3 (+, C4), 131.8 (+, C2’, C6’), 130.1 (+, C7), 129.4 (+, C8), 128.9 (+, C4’), 128.5 (+, C3’, C5’), 127.6 (+, C6’), 127.3 (+, C3), 127.3 (o, C4a), 122.6 (o, C1’), 117.5 (o, C3), 92.7 (o, Cβ), 86.7 (o, Cβ) ppm. IR (ATR): 3085, 3051, 3029, 2998, 2212, 1961, 1919, 1595, 1576, 1505, 1487, 1441, 1418, 1390, 1363, 1310, 1277, 1217, 1192, 1175, 1134, 1068, 1029, 919, 871, 846, 815, 756, 687, 641, 579, 550, 529, 506, 485, 442 cm−1. HRMS (ESI): m/z calcd for C17H12NNa [M + Na]+ 252.0789, found 252.0789.

4-(Phenylethynyl)quinoline (8c). According to Procedure 1, a solution of 0.624 g (3.00 mmol) of 4-bromoquinoline 6c, 0.042 g (0.06 mmol) of Pd(PPh3)2Cl2, 0.012 g (0.06 mmol) CuI and 0.367 g (3.60 mmol) of ethynylbenzene 7 in 20 mL of anhydrous NEt3 was heated over the period of 2 h under reflux temperature. Finally, a purification by column chromatography (petroleum ether:ethyl acetate = 5 : 1) gave 4-(phenylethynyl)quinoline 8c. Yield 0.674 g, 98%, of a yellow solid, m.p. 45 °C.1H NMR (600 MHz, CDCl3); δ = 8.90 (d, J = 4.4 Hz, 1H, 2-H), 8.38 (dd, J = 0.6, 1.4, 8.3 Hz, 1H, 5-H). 13C NMR (150 MHz, CDCl3); δ = 149.9 (+, C2), 148.3 (o, C8a), 131.2 (+, C2’, C6’), 130.0 (+, C7), 128.9 (o, C4), 129.5 (+, C4’), 128.7 (+, C3’, C5’), 127.9 (o, C4a), 127.3 (+, C6), 126.1 (+, C5), 123.7 (+, C3), 122.4 (o, C1’), 98.8 (o, Cβ), 85.2 (o, Cβ) ppm. IR (ATR): 3085, 3051, 3029, 2998, 2212, 1961, 1919, 1595, 1576, 1505, 1487, 1441, 1418, 1390, 1363, 1310, 1277, 1217, 1192, 1175, 1134, 1068, 1029, 919, 871, 846, 815, 756, 687, 641, 579, 550, 529, 506, 485, 442 cm−1. HRMS (ESI): m/z calcd for C19H11NNa [M + Na]+ 264.0969, found 264.0969.
General procedure of preparation of propeller-like compounds (Procedure 2)

Benzophenone (10 g) was added to a 50 mL round-bottomed flask fitted with an air condenser. Corresponding phenylethynylquinoline 8 (2.00 mmol) and tetraphenycyclopentadienone 9 (2.50 mmol) were added to the flask, which was heated for 0.5 h using a heat gun. The solution was cooled to rt and toluene (10 mL) was added to prevent the solidification of the benzophenone. After cooling, n-hexane (50 mL) was added, resulting in the precipitation of a product, which was collected by vacuum filtration.

2,3,4,5,6-Pentaphenyl-1-(quinolin-2-yl)benzene (10a).

2,3,4,5,6-Pentaphenyl-1-(quinoline-2-yl)benzene 10a was prepared by Procedure 2 using 2-(phenylethynyl)quinoline 8a (0.158 g, 0.690 mmol) and tetraphenycyclopentadienone 9 (0.394 g, 1.035 mmol) in benzophenone (5 g) in 10 mL round-bottomed flask in 0.75 h. Yield 0.260 g, 64%, a white solid, m.p. >360 °C. ^1H NMR (600 MHz, CDC13): δ = 7.75 [d, J = 8.6 Hz, 1H, 8ii-H], 7.64 [d, J = 8.5 Hz, 1H, 4ii-H], 7.55 [dd, J = 1.2, 8.2 Hz, 1H, 1ii-H], 7.51 [dd, J = 1.5, 6.9, 8.5 Hz, 1H, 7ii-H], 7.36 [dd, J = 1.1, 7.0, 8.1 Hz, 1H, 6ii-H], 7.01 (d, J = 8.5 Hz, 1H, 3ii-H), 7.00–6.96 (m, 2H, Ph), 6.93–6.83 (m, 16 H, 2ii-H, 4ii-H, 2iii-H, 6ii-H, 2iv-H, 6iv-H, 3iii-H, 5ivii-H, 3ivii-H, 5iv-H, 3vii-H, 5vii-H, 3viii-H, 5viii-H), 6.79–6.72 (m, 7H, Ph) ppm. ^13C NMR (150 MHz, CDC13): δ = 160.2 (o, C2ii), 147.1 (o, C8ai), 141.6 (o, C1vii), 140.8/140.4/140.1/140.1 (o, C2, C3, C5, C6, C1i, C1ii, C1v, C1vi), 140.6 (o, C4), 140.0 (o, C1), 134.2 (+, C4ii), 131.7/131.5/131.4/130.7 (+, Ph), 129.5 (+, C7), 129.0 (+, C8ii), 127.3 (+, C5v), 126.8 (Ph), 126.0 (+, C6ii), 125.7 (o, C4ai), 125.1/125.45 (+, Ph) ppm. IR (ATR): 3055, 3025, 2957, 1597, 1585, 1501, 1441, 1403, 1323, 1300, 1221, 1154, 1073, 1029, 948, 839, 812, 753, 718, 695, 617, 583, 555, 531, 478 cm⁻¹. HRMS (ESI): m/z calc'd for C43H32N+[M+H]⁺ 586.2530, found 586.2531.

2,3,4,5,6-Pentaphenyl-1-(quinolin-3-yl)benzene (10b).

2,3,4,5,6-Pentaphenyl-1-(quinoline-3-yl)benzene 10b was prepared by Procedure 2 using 3-(phenylethynyl)quinoline 8b (0.458 g, 2.00 mmol) and tetraphenyldicyclopentadienone 9 in 50 mL round-bottomed flask in 0.5 h. Yield 0.590 g, 51%, a white solid, m.p. 334 °C. ^1H NMR (600 MHz, CDCl3): δ = 8.45 [d, J = 2 Hz, 1H, 1ii-H], 7.84 [d, J = 8.4 Hz, 1H, 8ii-H], 7.59 [d, J = 2 Hz, 1H, 1iv-H], 7.53–7.51 (m, 1H, 7ii-H), 7.43 (d, J = 8.0 Hz, 5ii-H), 7.35–7.33 (m, 1H, 6ii-H), 6.88–6.85 (m, 20H, 2ii-H, 4ii-H, 2iii-H, 6ii-H, 2iv-H, 6iv-H, 3ii-H, 5ivii-H, 3ivii-H, 5iv-H, 3vii-H, 5vii-H, 3viii-H, 5viii-H, 3viii-H, 5vii-H), 6.83–6.78 (m, 4H, 4iv-H, 4ii-H, 4iv-H, 4vii-H), 6.78–6.77 (m, 1H, 1iv-H) ppm. ^13C NMR (150 MHz, CDCl3): δ = 152.1 (+, C2i), 147.1 (o, C8ai), 138.5 (+, C4), 132.3 (+, C3ii, C5ii), 131.7 (+, C2ii, C6ii), 130.4 (+, C7), 129.6 (+, C8ii), 127.8 (+, C5v), 127.5 (+, C6ii), 127.4 (o, C4ai), 123.2 (o, C1ii), 122.6 (o, C4ii), 117.4 (o, C3), 92.1 (o, C6ii), 88.7 (o, C4), 83.2 (o, C6v), 79.4 (o, C6v) ppm. IR (ATR): 3265, 3060, 3034, 2101, 1906, 1791, 1699, 1602, 1566, 1487, 1404, 1351, 1266, 1145, 1105, 1010, 981, 958, 906, 861, 838, 782, 752, 691, 653, 622, 548, 471, 419 cm⁻¹. HRMS (ESI): m/z calc'd for C48H32N+[M+H]⁺ 594.2694, found 594.2692; m/z calc'd for C48H31Na+[M+Na]⁺ 276.0789, found 276.0785.

1-(Quinolin-3-yl)-2,3,4,5-tetraphenyl-6-(4-(1,2,3,4-tetraphenylphenyl)phenyl)-benzene (15).

1-(Quinolin-3-yl)-2,3,4,5-tetraphenyl-6-(4-(1,2,3,4-tetraphenylphenyl)phenyl)-benzene 15 was prepared by Procedure 2 using 4-(1-ethylthiophenyl)quinoline 8c (0.290 g, 1.146 mmol) and tetraphenycyclopentadienone 9 (1.320 g, 3.438 mmol, 3.0 equiv.) in benzophenone (10 g) in 50 mL round-bottomed flask in 0.5 h. Yield 0.885 g, 77%, a
brown solid, m.p. 368 °C (decomp.). $^1$H NMR (600 MHz, CDCl$_3$): $\delta$ = 8.42 (d, J = 2.0 Hz, 1H), 7.90 (d, J = 8.3 Hz, 1H), 7.57 (ddd, J = 1.4, 6.8, 8.3 Hz, 1H), 7.55 (d, J = 2.0 Hz, 1H), 7.46–7.45 (m, 1H), 7.41–7.38 (m, 1H), 7.23 (s, 1H), 7.15–7.13 (m, 2H), 7.07–7.06 (m, 2H), 6.94–6.55 (m, 40H) ppm. $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ = 152.9 (+), 145.7 (o), 141.8 (o), 141.7 (o), 141.3 (o), 141.1 (o), 140.86 (o), 140.82 (o), 140.80 (o), 140.73 (o), 140.48 (o), 140.43 (o), 140.34 (o), 140.27 (o), 140.21 (o), 140.07 (o), 139.95 (o), 139.7 (o), 139.3 (o), 139.1 (o), 138.8 (o), 137.9 (o), 137.8 (+), 136.5 (o), 134.2 (o), 132.5 (+), 131.6 (+), 131.5 (+), 131.39 (+), 131.35 (+), 131.0 (+), 130.9 (+), 130.0 (+), 129.1 (+), 128.89 (+), 128.87 (+), 128.77 (+), 128.4 (+), 127.69 (+), 127.62 (+), 127.3 (+), 127.1 (+), 127.0 (+), 126.96 (o), 126.82 (+), 126.76 (+), 126.66 (+), 126.31 (+), 126.2 (+), 125.8 (+), 125.64 (+), 125.55 (+), 125.50 (+), 125.46 (+), 125.36 (+) ppm. IR (ATR): 3061, 2169, 1839, 1616, 1565, 1487, 1468, 1413, 1357, 1291, 1226, 1192, 911, 995, 906, 878, 869, 786, 770, 761, 748, 737, 640, 614, 594, 553, 527, 491, 479, 472, 461, 445, 415 cm$^{-1}$. MS (ESI): m/z = 281.1 [M + H]$^+$. HRMS (ESI): m/z calc for C$_{26}$H$_{11}$NaN$_3$ [M + Na]$^+$ 281.1074, found 281.1072.

3-[Quinolin-4-ylethynyl]quinoline (18b). According to Procedure 1, a solution of 0.208 g (1.00 mmol) of 3-bromoquinoline 6b, 0.007 g (0.01 mmol) of Pd(PPh$_3$)$_2$Cl$_2$, 0.0038 g (0.02 mmol) CuI and 0.218 g (1.05 mmol) of 3-ethylnylquinoline 17 in 10 mL of anhydrous NEt$_3$ was heated (2 h) under reflux temperature. Finally, a purification by column chromatography (petroleum ether: ethyl acetate = 3:1) gave 3-[quinolin-4-ylethynyl]quinoline 18b. Yield 0.196 g, 70%, a brownish solid, m.p. 173 °C.

$^1$H NMR (600 MHz, CDCl$_3$): $\delta$ = 9.05 (d, J = 2 Hz, 2H, 2'H), 8.36 (d, J = 2 Hz, 2H, 4'H, 4'H), 8.12 (d, J = 8.1 Hz, 2H, 8'H, 8'H), 7.82 (d, J = 8.3 Hz, 2H, 5'H, 5'H), 7.74 (ddd, J = 1.4, 6.9, 8.4 Hz, 2H, 7'H, 7'H), 7.58 (m, 4H), 7.58 (m, 4H) ppm. $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta$ = 152.0 (+, C2, C2'), 147.2 (o, C8a, C8a'), 138.8 (+, C4, C4'), 130.8 (+), 129.6 (+, C8, C8'), 127.8 (+, C5, C5'), 127.6 (+, C6, C6'), 127.3 (o, C4a, C4a'), 116.9 (o, C3, C3'), 90.0 (o, C4) ppm. IR (ATR): 3061, 2169, 1839, 1616, 1565, 1487, 1468, 1413, 1357, 1291, 1226, 1192, 911, 995, 906, 878, 869, 786, 770, 761, 748, 737, 640, 614, 594, 553, 527, 491, 479, 472, 461, 445, 415 cm$^{-1}$. MS (ESI): m/z = 281.1 [M + H]$^+$, HRMS (ESI): m/z calc for C$_{26}$H$_{11}$NaN$_3$ [M + H]$^+$ 281.1074, found 281.1072.

1-(Quinolin-3-yl)-2-(quinolin-4-yl)-3,4,5,6-tetraphenylbenzene (19b). 1-(Quinolin-3-yl)-2-(quinolin-4-yl)-3,4,5,6-tetraphenylbenzene 19b was prepared by Procedure 2 using 4-(quinolin-3-yl)ethynylquinoline 18b (0.264 g, 0.943 mmol) and tetraphenycyclopentadienide 9 (0.543 g, 1.414 mmol) in benzophenone (5 g) in 10 mL round-bottomed flask in 0.5 h. The solution was cooled to rt and tolune (3 mL) was added to prevent the solidification of the benzophenone. After cooling, n-hexane (200 mL) was added, resulting in the precipitation of 19b as a white powder, which was washed with n-hexane and toluene, and collected by vacuum filtration. Yield 0.570 g, 90%, a white solid, m.p. 344 °C.

$^1$H NMR (600 MHz, DMSO$_{d$_6$}$), two sets of isomeric rotamer forms (1:0.8): $\delta$ = 8.52 (d, J = 2.1 Hz, 3.6H, 2-H, 2'-H), 7.97 (d, J = 1.7 Hz, 2H, 2'-H), 7.93 (d, J = 1.7 Hz, 1.6H, 4'-H), 7.64–7.61 (m, 3.6H, 8-H, 8'-H), 7.59 (d, J = 7.9 Hz, 2H, 5-H), 7.52 (d, J = 8.3 Hz, 1.6H, 5'-H), 7.50–7.47 (m, 3.6H, 7-H, 7'-H), 7.38–7.36 (m, 2H, 6-H, 6'-H), 7.35–7.32 (m, 1.6H, 6'-H), 7.01–6.74 (m, 36H, Ph) ppm. $^{13}$C NMR (150 MHz, DMSO$_{d$_6$}$): $\delta$ = 152.0 (+, C2), 151.8 (+, C2'), 144.99 (o, C8a'), 144.98 (o, C8), 141.06 (o), 141.04 (o), 139.09 (+), 139.32 (o), 137.24 (+, C4), 137.0 (+, C4'). Yield 0.469 g, 78%, a white solid, m.p. 368 °C (decomp.).
Evaporation of the solvent chloromethane and filtered through a short pad of silica gel. The resulting residue was dissolved in anhydrous dioxane (4 mL) in an oven dried Schlenk vessel. 2-(Phenylethynyl)quinoline

\[ 2-(\text{Phenylethynyl})\text{quinoline} \]

was evaporated. IR (ATR): 3058, 3038, 3007, 1617, 1595, 1501, 1443, 1424, 1332, 1305, 1253, 1223, 1156, 1139, 1113, 1073, 1031, 959, 906, 838, 753, 698, 619, 587, 515, 476, 431, 423, 412 cm\(^{-1}\). HRMS (ESI): m/z calc for C\(_{48}\)H\(_{35}\)N\(_2\) [M H\(^+\)] 637.2639, found 637.2629.

**General procedure for the synthesis of substituted benzenes**

(Procedure 3)

2-(Phenylethynyl)quinoline 8a (0.21 g, 0.92 mmol) was dissolved in anhydrous dioxane (4 mL) in an oven dried Schlenk flask under nitrogen atmosphere and the flask was evacuated and filled with nitrogen repeatedly (3×). Then, Co\(_2\)(CO)\(_8\) (0.015 g) was added to the flask under a nitrogen atmosphere and the flask was evacuated and filled with nitrogen again (3×). The resulting mixture was refluxed for 14 h and dioxane was evaporated. The resulting residue was dissolved in dichloromethane and filtered through a short pad of silica gel. Evaporation of the solvent afforded a dark colored solid which was purified by column chromatography with PE–EE as eluent.

1,3,5-Triphenyl-2,4,6-tri(quinolin-2-yl)benzene (20a).

Yield 0.021 g, 10%, a white solid, m.p. 337 °C. \(^1\)H NMR (600 MHz, DMSO-d\(_6\)): \( \delta = 7.83 \) (d, \( J = 8.5 \) Hz, 3H, 4′-H), 7.72 (d, \( J = 8.5 \) Hz, 3H, 5′-H), 7.67 (d, \( J = 9.7 \) Hz, 3H, 5′-H), 7.57 (t, \( J = 7.3 \) Hz, 3H, 7′-H), 7.41 (t, \( J = 7.3 \) Hz, 3H, 6′-H), 7.22 (d, \( J = 8.5 \) Hz, 3H, 3′-H), 7.05 (br s, 6H, 2″-H, 6″-H), 6.70 (br s, 6H, 3″-H, 5″-H), 6.63 (t, \( J = 7.3 \) Hz, 3H, 4″-H) ppm. \(^{13}\)C NMR (150 MHz, DMSO-d\(_6\)): \( \delta = 158.9 \) (o, C2′), 146.4 (o, 8a′), 139.9 (o, C2, C4; C6), 139.8 (o, C1, C3, C5), 138.7 (o, C1″), 134.1 (+, C4′), 130.6 (+, C2″, C6″), 129.0 (+, C7′), 128.6 (+, C8′), 127.4 (+, C5′), 126.3 (+, C3″, C5″), 126.1 (+, C6″), 125.8 (+, C4″), 125.4 (o, C4′a), 124.2 (+, C3′) ppm. IR (ATR): 3058, 3038, 3007, 1617, 1595, 1501, 1443, 1424, 1332, 1305, 1253, 1223, 1156, 1139, 1113, 1073, 1031, 959, 906, 838, 753, 698, 619, 587, 515, 476, 431, 423, 412 cm\(^{-1}\). MS (ESI): m/z = 688.5 [M + H\(^+\)]. HRMS (ESI): m/z calc for C\(_{53}\)H\(_{34}\)N\(_3\) [M H\(^+\)] 688.2745, found 688.2743.

**General procedure for the preparation of the salts**

(Procedure 4)

Samples of 0.50 mmol of the corresponding quinolines were dissolved in toluene containing 1 drop of nitrobenzene. Then 0.75 mmol of dimethyl sulfate was added with stirring. Thereafter the resulting mixture was stirred under reflux temperature. After completion of the reaction (controlled by TLC), the solution was cooled, the crude product was filtered off, washed with ethyl acetate (3 × 10 mL), and dried to afford the product.

2,3,4,5,6-Pentaphenyl-1-(1-methylquinolinium-2-yl)benzene methylsulfate (22a). According to Procedure 4, a solution of 0.100 g (0.171 mmol) of 2,3,4,5,6-pentaphenyl-1-(quinoline-2-yl)benzene 10a, 1 drop of nitrobenzene and 0.06 mL (0.63 mmol) of dimethyl sulfate in 5 mL of anhydrous toluene was heated for 2 h under reflux temperature to give 2,3,4,5,6-pentaphenyl-1-(1-methylquinolinium-2-yl)benzene methylsulfate 22a. Yield 0.115 g, 95%, a white solid, m.p. 190 °C. \(^1\)H NMR (600 MHz, DMSO-d\(_6\)): \( \delta = 8.88 \) (d, \( J = 8.5 \) Hz, 1H, 4′-H), 8.31 (d, \( J = 9.0 \) Hz, 1H, 8′-H), 8.24–8.23 (m, 2H, 3′-H, 5′-H), 8.14 (t, \( J = 8.0 \) Hz, 7′-H), 7.93 (t, \( J = 7.4 \) Hz, 6′-H), 7.10–6.84 (m, 25H, Ph), 4.41 (s, 3H, N(CH\(_3\))\(_2\)), 3.38 (s, 3H, CH\(_3\)SO\(_3\)) ppm. \(^{13}\)C NMR (150 MHz, DMSO-d\(_6\)): \( \delta = 159.1 \) (o, C2′), 144.2 (+, C4′), 143.9 (o, C1), 141.2 (o), 139.1 (o), 138.9 (o), 138.3 (o), 137.5 (o, C8′a), 137.4 (o), 136.0 (+, C7′), 131.7 (+), 130.9 (+), 130.6 (+), 130.4 (+), 130.4 (+, C6), 130.3 (+, C5), 130.26 (+), 130.0 (+), 129.3 (+), 126.7 (+), 127.43 (o, C4′a), 127.39 (+, C3′), 127.2 (+), 126.95 (+), 126.91 (+), 126.86 (+), 126.2 (+), 126.0 (+), 119.1 (+, C8′), 52.8 (+, CH\(_3\)SO\(_3\)), 42.5 (+, N(CH\(_3\))\(_2\)) ppm. IR (ATR): 3056, 3023, 1619, 1600, 1577, 1519, 1497, 1442, 1409, 1347, 1252, 1224, 1176, 1152, 1073, 1059, 1013, 918, 849, 817, 770, 756, 723, 698, 644, 608, 576, 554, 532, 428 cm\(^{-1}\). HRMS (ESI): m/z calc for C\(_{64}\)H\(_{43}\)N\(_2\)O\(_3\) [M + H\(^+\)] 863.2899, found 863.2896.
Ph), 7.02 (d, J = 1.5, 7.1, 8.8, 1H, 7-H), 8.06 (dd, J = 1.1, 8.4, 1H, 5-H), 7.92–7.90 (m, 1H, 6-H), 7.05 (d, J = 7.7 Hz, 2H, Ph), 7.02 (d, J = 7.7 Hz, 2H, Ph), 6.96–6.82 (m, 2H, Ph), 4.34 (s, 3H, NCH3), 3.37 (s, 3H, CH3SO4) ppm. 13C NMR (150 MHz, DMSO-d6): δ = 150.6 (+), 147.5 (+), 144.2 (o), 140.7 (+), 139.0 (o), 138.4 (o), 135.35 (o, C8a), 135.48 (+, C7), 134.4 (o, C3), 132.8 (o, C1′), 131.0 (+), 130.7 (+), 130.64 (+), 130.60 (+), 130.54 (+), 130.5 (+, C6), 129.9 (+, C5), 127.7 (+, C4a), 127.4 (+), 126.89 (+), 126.67 (+), 126.77 (+), 126.4 (+), 126.45 (+), 125.92 (+), 125.75 (+, 118.9 (+, C8), 52.8 (+, CH3SO4), 44.8 (+, NCH3) ppm. IR (ATR): 3051, 3023, 2961, 1600, 1524, 1494, 1462, 1378, 1254, 1215, 1063, 1012, 760, 697, 618, 577, 558, 441 cm⁻¹. HRMS (ESI): m/z calcd for C46H34N⁺ [M]+ 600.2686, found 600.2687.

2,3,4,5,6-Pentaphenyl-1-(1-methylquinolinium-4-yl)benzene methylsulfate (22c). According to Procedure 4, a solution of 0.154 g (0.263 mmol) of 2,3,4,5,6-pentaphenyl-1-(quinoline-4-yl)benzene 10c, 1 drop of nitrobenzene and 0.06 mL (0.63 mmol) of dimethyl sulfate in 5 mL of anhydrous toluene was heated for 2 h under reflux temperature to give 2,3,4,5,6-pentaphenyl-1-(1-methylquinolinium-4-yl)benzene methylsulfate 22c. Yield 0.185 g, 99%, a brownish solid, m. p. 355 °C (decomp.). 1H NMR (600 MHz, DMSO-d6): δ = 9.14 (d, J = 6.0 Hz, 1H, 2-H), 8.27 (dd, J = 1.0, 8.4 Hz, 1H, 5-H), 8.20 (d, J = 8.9 Hz, 1H, 8-H), 8.15 (d, J = 6.0 Hz, 1H, 3-H), 8.11 (dd, J = 1.4, 7.1, 8.7 Hz, 1H, 7-H), 7.96–7.94 (m, 1H, 6-H), 7.06 (d, J = 7.7 Hz, 2H, Ph), 7.01 (d, J = 7.7 Hz, 2H, Ph), 6.95–6.83 (m, 14H, Ph), 6.74–6.71 (m, 4H, Ph), 6.60–6.57 (m, 2H, Ph), 4.42 (s, 3H, NCH3), 3.37 (s, 3H, CH3SO4) ppm. 13C NMR (150 MHz, DMSO-d6): δ = 158.5 (o, C4), 147.5 (+, C2), 142.3 (o, 140.6 (o), 139.36 (o), 139.34 (o), 139.8 (o), 139.33 (o), 137.1 (o, C8a), 135.7 (+, C7), 133.1 (o, C6a), 131.0 (+), 130.8 (+), 130.52 (+), 129.49 (+), 129.83 (+, C6), 128.80 (+), 129.3 (+, C5), 128.3 (o, C4a), 126.83 (+), 126.78 (+), 126.74 (+, 126.71 (+), 126.67 (+), 126.64 (+), 125.81 (+), 125.77 (+), 125.3 (+, C3), 118.8 (+, C8), 52.8 (+, CH3SO4), 45.0 (+, NCH3) ppm. IR (ATR): 3051, 3023, 2961, 1600, 1524, 1494, 1462, 1378, 1254, 1215, 1063, 1012, 760, 697, 618, 577, 558, 441 cm⁻¹. HRMS (ESI): m/z calcd for C46H34N⁺ [M]+ 600.2686, found 600.2673.

1-(1-Methylquinolinium-3-yl)-2,3,4,5-tetraphenyl-6-(4,1,2,3,4-tetraphenyl)benzene hexafluorophosphate (23PF6). A suspension of 0.050 g (0.046 mmol) of 1-(1-methylquinolinium-3-yl)-2,3,4,5-tetraphenyl-6-(4,1,2,3,4-tetraphenyl)benzene methylsulfate 23 and 0.008 g (0.049 mmol) of NH4PF6 in 4 mL of water was stirred for 1 day at rt to give 1-(1-methylquinolinium-3-yl)-2,3,4,5-tetraphenyl-6-(4,1,2,3,4-tetraphenyl)benzene hexafluorophosphate 23PF6. Yield 0.049 g, 95%, a yellow solid, m. p. 220 °C (decomp.). 1H NMR (600 MHz, DMSO-d6): δ = 9.28 (s, 1H, Q), 8.73 (s, 1H, Q), 8.35 (d, J = 8.9 Hz, 1H, Q), 8.20 (d, J = 7.7 Hz, 1H, Q), 8.05 (d, J = 7.9 Hz, 1H, Q), 7.96 (t, J = 7.5 Hz, 1H, Q), 7.26 (m, 1H, Ph), 7.17–7.14 (m, 4H, Ph), 7.02–6.47 (m, 40H, Ph), 4.33 (s, 3H, NCH3) ppm. 13C NMR (150 MHz, DMSO-d6): δ = 150.6 (+), 147.5 (+), 142.2 (o), 141.5 (o), 140.9 (o), 140.7 (o), 140.4 (o), 140.3 (o), 140.0 (o), 139.6 (o), 139.3 (o), 139.01 (o), 138.96 (o), 138.8 (o), 138.4 (o), 137.3 (o), 136.5 (o), 135.6 (o), 135.5 (o), 134.4 (o), 132.8 (o), 131.0 (o), 130.9 (+), 130.8 (+), 130.7 (+), 130.64 (+), 130.60 (+), 130.55 (+), 130.53 (+), 130.44 (+), 130.36 (+), 130.28 (+), 130.0 (+, 129.4 (+), 128.9 (+), 1286 (+), 128.4 (+), 128.2 (+), 127.3 (+), 127.0 (+), 126.85 (+), 126.81 (+), 126.51 (+), 126.46 (+), 126.4 (+), 125.91 (+), 125.85 (+), 125.8 (+), 125.44 (+), 125.37 (+), 125.31 (+), 118.9 (+), 52.7 (+), 44.8 ppm. IR (ATR): 3055, 3023, 1600, 1524, 1442, 1378, 1249, 1222, 1178, 1157, 1138, 1058, 1008, 911, 852, 797, 766, 697, 565, 496, 432 cm⁻¹. HRMS (ESI): m/z calcd for C76H52N6 [M]+ 980.4251, found 980.4257.

1,2-Di-(1-methylquinolinium-3-yl)-3,4,5,6-tetraphenylbenzene dihexafluorophosphate (24a). A solution of 0.050 g (0.079 mmol) of 1,2-di-(quinoline-3-yl)-3,4,5,6-tetraphenylbenzene 19a, 1 drop of nitrobenzene and 0.02 mL (0.21 mmol) of dimethyl sulfate in 5 mL of anhydrous toluene was heated for 3 h under reflux temperature, cooled to rt and extracted with water (3 × 5 mL) and precipitated with excess of NH4PF6.
(1.3 equiv.) to give 1,2-di(1-methylquinolinium-3-yl)-3,4,5,6-tetraphenylbenzene dihexafluorophosphate (24a). Yield 0.068 g, 90%, a white solid, m.p. 240 °C. \(^1\)H NMR (600 MHz, DMSO-d\(_6\)), two sets of isochronous rotameric forms (0.9 : 1):

\[
\delta = 9.43 \text{ (d, } J = 1.3 \text{ Hz, 1H, 2-H), 9.40 \text{ (d, } J = 1.3 \text{ Hz, 1H, 2-H), 9.05 \text{ (s, 1H, 4' -H), 8.88 \text{ (s, 0.9H, 4-H), 8.30 \text{ (d, } J = 8.8 \text{ Hz, 1H, 8'-H), 8.27 \text{ (d, } J = 8.9 \text{ Hz, 9H, 8'-H), 8.16–8.09 \text{ (m, 3.8H, 5-H, 5'-H, 6-H, 7-H, 7'-H), 7.93–7.90 \text{ (m, 1.9H, 6-H, 6'-H), 7.05–6.84 \text{ (m, 48H, Ph), 4.38 \text{ (s, 6H, N'CH}_3\text{), 4.32 \text{ (s, 5.4H, NCH}_3\text{)} ppm.} \]

\(^{13}\)C NMR (150 MHz, DMSO-d\(_6\)): \(\delta = 150.6 \text{ (+, C2), 149.8 \text{ (+, C2'), 147.9 \text{ (+, C4), 147.6 \text{ (+, C4), 142.8 \text{ (o), 142.7 \text{ (o), 141.9 \text{ (o), 141.8 \text{ (o), 138.5 \text{ (o), 137.6 \text{ (o), 136.5 \text{ (o, C8a), 136.4 \text{ (o, C8a), 135.94 \text{ (+, C7 or C7'), 135.85 \text{ (+, C7 or C7'), 133.10 \text{ (o, C6), 128.99 \text{ (o, C6), 132.4 \text{ (o), 132.2 \text{ (o), 130.89 \text{ (+), 130.75 \text{ (+), 130.69 \text{ (+), 130.60 \text{ (+), 130.48 \text{ (+), 130.44 \text{ (+), 130.42 \text{ (+), 130.38 \text{ (+), 130.33 \text{ (+), 130.31 \text{ (+), 130.22 \text{ (+, C5), 130.07 \text{ (+, C5'), 129.72 \text{ (o, C4a), 127.89 \text{ (o, C4a), 127.6 \text{ (+), 127.0 \text{ (+), 126.7 \text{ (+), 126.3 \text{ (+), 119.00 \text{ (+, C8'), 118.90 \text{ (+, C8), 45.4 \text{ (+, NCH}_3\text{), 45.2 \text{ (+, NCH}_3\text{) ppm.} \)} \]

IR (ATR): 3057, 3027, 1631, 1602, 1583, 1523, 1497, 1443, 1380, 1356, 1334, 1230, 1137, 1144, 1115, 1073, 1024, 936, 830, 760, 744, 702, 619, 556, 524, 504, 419 cm\(^{-1}\). HRMS (ESI): m/z caleed for C\(_{50}H_{38}N_2\) [M\(^{+}\)]\(^{+}\) 333.1512, found 333.1518.

1-(1-Methylquinolinium-3-yl)-2-(1-methylquinolinium-4-yl)-3,4,5,6-tetraphenylbenzene dihexafluorophosphate (24b). A solution of 0.050 g (0.079 mmol) of 1-(quinoline-3-yl)-2-(quinoline-4-yl)-3,4,5,6-tetraphenylbenzene (19b), 1 drop of nitrobenzene and 0.10 mL of dimethyl sulfate in 5 mL of anhydrous toluene was heated for 3 h under reflux temperature. When the obtained salt was dissolved in water and precipitated with 1.05 equiv. of NH\(_4\)PF\(_6\) to give hexakis(1-methylquinolinium-3-yl)benzene hexakis-hexafluorophosphate 25. Yield 0.171 g, 95%, a white solid, m.p. 195 °C (decomp.). \(^1\)H NMR (600 MHz, DMSO-d\(_6\)): \(\delta = 9.41–8.89 \text{ (m, 12H), 8.34–8.16 \text{ (m, 18H), 8.00–7.92 \text{ (m, 6H), 4.44–4.28 \text{ (m, 18H) ppm.} \)} \]

\(^{13}\)C NMR (150 MHz, DMSO-d\(_6\)): \(\delta = 148.7, 148.2, 137.9, 137.8, 137.7, 137.5, 137.0, 131.0, 130.4, 128.6, 128.0, 119.4, 45.97, 45.89, 45.85, 45.79 ppm. IR (ATR): 3084, 1631, 1582, 1524, 1451, 1382, 1228, 1173, 1040, 952, 920, 827, 771, 753, 740, 614, 556, 494, 440, 413 cm\(^{-1}\). \]

Conflicts of interest

There are no conflicts to declare.

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