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Ethynyl-Bridged Bis-quinolinium Dyes: Studies of the Dependence of Different Types of Conjugation on Spectroscopic Properties

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Dicationic bis-quinolinium salts possessing different types of conjugation are presented in which the hetareniums are separated by acetylenic or 1,4-diethynylbenzene spacers. Cross-conjugation is induced by interconnections via the 3-positions of the heteroareniums, and conjugation is realized by 2,2/2,4/4,4-interconnections. We also synthesized mixed cross-conjugated/conjugated 2,3/4,3-interconnected species. The different types of conjugation determine the charge distribution according to the rules of resonance which translate into characteristic ^{13}C NMR as well as UV-Vis-spectroscopic properties, LUMO geometries, and chemical properties. We found that the triple bond's resonance frequencies are sensitive ^{13}C NMR spectroscopic indicators for the type of conjugation. Combining cross-conjugated and conjugated structure elements of dicationic bis-quinolinium dyes via triple bonds without additional benzene spacer results in considerable bathochromic shifts of the UV-Vis absorption maxima [$\Delta\lambda_{max} \approx 100$ nm]. A charge transfer was calculated from the HOMO of the conjugated into the LUMO of the cross-conjugated partial structure.

Introduction

The type of conjugation strongly influences the chemical and physical properties of π-electronic systems. For example, cross-conjugated[1] hydrocarbons are branched conjugated molecules.[2] In contrast to their linear conjugated isomers, cross-conjugated π-electron systems are believed to have a more fragmented electronic connection and a more restricted delocalization.[3] For example, cross-conjugated dendralenes, as opposed to linear polyenes, exhibit notable inhibitions of the delocalization in the case of polyenes and related hydrocarbons. Thus, they can be regarded as groups of isolated butadiene units.[2a]

Much effort is currently directed toward a deeper understanding of the differences between linear conjugation and cross-conjugation of organic molecules, and viewpoints from computational chemistry,[4] materials chemistry,[5] heteroelement chemistry (see phenylene-bridged 1,2,3-trisilacyclopentadienes),[6] polymer chemistry,[7] and mathematics[8] have been combined, compared, and published. In light of the results achieved to date, it was expressed that researchers have only begun to unravel the full picture of cross-conjugation.[4f]

Delocalization of positive and negative charges in π-electronic systems is widely discussed concerning heterocyclic mesomeric betaines (HMBs). As the name suggests, the original classification of HMBs is based on the rules of resonance. Depending on the positions where the charges are located in a molecule, three major types of *conjugation* (in *italic*, to distinguish them from classic conjugation types) have been identified (*conjugation*, *cross-conjugation*, *pseudo-cross-conjugation*) from which three classes of HMBs are derived.[9] The identification of characteristic dipole types as well as isoconjugation relationships to odd and even alternant and non-alternant hydrocarbon equivalents supported this classification. Recently, a connectivity-matrix analysis expanded the original classification,[10] so that *conjugated*, *cross-conjugated*, *pseudo-cross-conjugated*, *semi-conjugated*, and *pseudo-semi-conjugated* mesomeric betaines can be distinguished. The classification, which undoubtedly leads to a deeper understanding of the chemistry and physics of mesomeric betaines, gives an idea of how complicated the phenomenon of conjugation is. The delocalization of charges can be discussed in association with any π-electronic system with one or more charges, as different properties of the compounds arise depending on their type of conjugation. For example, most monocharged organic dyes are designed in such a way that the charge is delocalized over the entire π-electronic system. In other words, cross-conjugated branches are avoided to get the maximum profit from a

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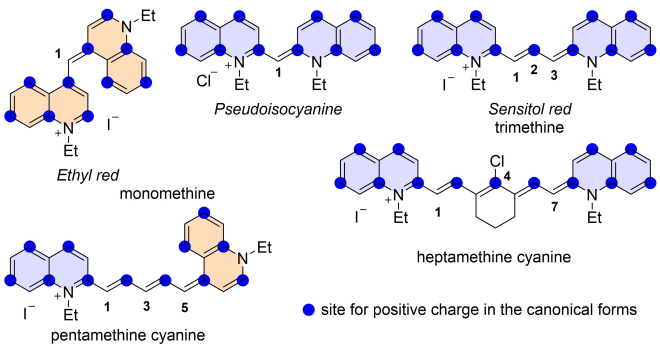
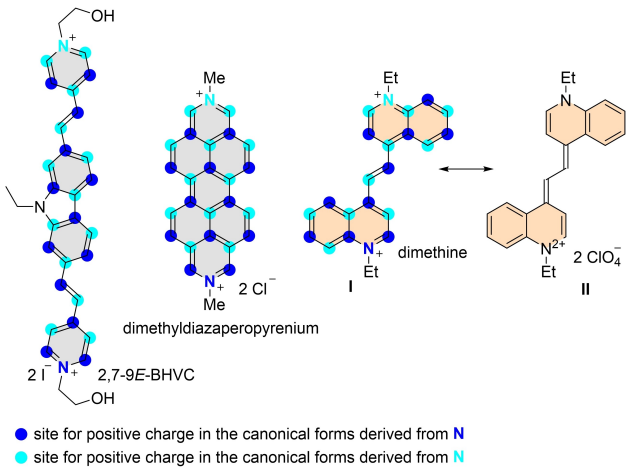
designed molecule. Thus, the formation of salts is an essential step in the synthesis of cyanine dyes,[11] in which quinoline end-groups are connected via 2- and 4-positions of the quinoline ring. Cross-conjugated connections via the 3-position seemingly are unknown (Scheme 1). Most cyanine dyes differ in the length of the conjugated carbon chain, whereas the quinolinium positions remain the same. Therefore, they are classified as mono-, tri-, and pentamethine derivatives.

In dyes with an extended π-electronic system that possess two positive charges such as 2,7-9*E*-BHVC[12] or dimethyldiazaperopyrenium dichloride,[13] charges are also delocalized so that all carbons of a system are sites of positive charges according to the rules of resonance, respectively (Scheme 2). The same is true for a dimethine cyanine analog, which, in contrast to its parent dyes, is a dicationic molecule.

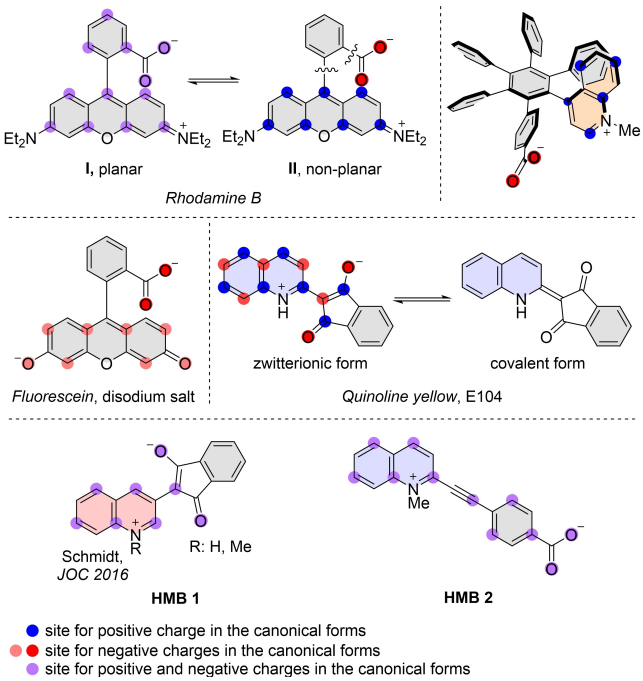
Additionally, the representation of the dimethine, in which a „2+" charge is located on one nitrogen atom (structure **II**) seems less favorable than the „common" one (structure **I**), where each nitrogen atom bears one charge. Nevertheless, **II** is an allowed resonance form according to the rules of resonance which reflects the delocalization of the positive charges over the entire π-electron system, similar to all monocationic structures shown in Scheme 1. *Rhodamine B* or the disodium salt of *fluorescein*, examples of widely known dyes, also possess two charges in their π-systems (Scheme 3). In the case of *rhodamine B*, both positive and negative charges have common sites of delocalization in the planar conformation **I**, when electron sextet structures possessing an O^+ in the carboxylate group are taken into consideration. These canonical forms are characteristic of *pseudo-cross-conjugated* mesomeric betaines.[9][14] However, torsions of the carboxylate group and the phenyl ring can interrupt the π-conjugation and cause a charge separation as typical for *cross-conjugated* mesomeric betaines.[9] The same idea was used by us for the preparation of molecular propellers, in which two charges were placed on the neighboring wings of hexaaryl benzene.[9b] For *fluorescein*, the negative charges are separated by cross-conjugation, however, as for *rhodamine B*, one of two charges is distributed on the xanthene core. Introducing positive and negative charges in xanthene will result in a neutral molecule. A known example of such a combination is *Quinoline yellow*, which - despite its zwitterionic representation - also has a fully covalent form. We already reported about its analog (**HMB 1**), in which the indandione ring is connected to position 3 of the quinolinium ring. As the molecule is represented exclusively by dipolar structures, it is a member of the substance class of heterocyclic mesomeric betaines. It is interesting to note that the delocalization of the positive charge of 3-substituted quinolinium salts is exclusively restricted to the quinolinium ring (even if a conjugated substituent is attached) unless charges are installed in a conjugated substituent in this position. An example is **HMB 1** which has an anionic indandione ring. In this case, the positive charge can be delocalized into the indandione substituent



Scheme 1. Some examples of quinoline-containing cyanine dyes. Blue circles indicate positions of positive charge delocalization according to the rules of resonance. Numbers indicate the numbers of connecting methine groups between the aromatics.



Scheme 2. Examples of dicationic dyes. Charge distribution according to the rules of resonance.



Scheme 3. Examples of dyes and molecules which possess two charges.

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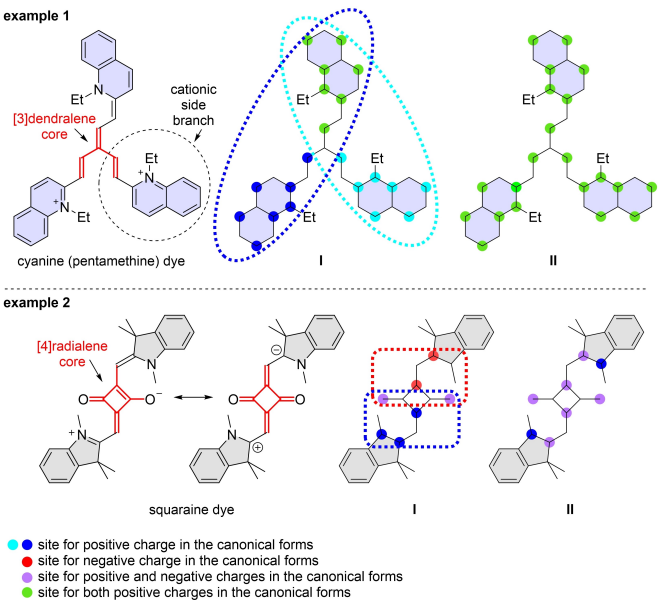
according to the rules of resonance and, as a result, common sites for either charge exist in the canonical formulae. Cross-conjugated salts can thus be transformed into *conjugated mesomeric betaines*. *Vice versa*, the negative charge of carboxylate groups of *pseudo-cross-conjugated mesomeric betaines* such as **HMB 2** can formally be delocalized into the entire π-electron system when the aforementioned electron-sextet structures of one of the oxygen atoms are taken into consideration. As a result, for both presented molecules **HMB 1** and **HMB 2** one of the charges creates additional sites of delocalization to another one, which was originally in cross-conjugation.

This phenomenon can be visualized by two other prominent examples of organic dyes (Scheme 4), where it translates into spectroscopic properties. The first example is a pentamethine dye[15] with an additional cationic side branch. The positive charges can be delocalized exclusively in two quinolinium rings, respectively, resulting in a charge distribution as displayed by **I**. The ^{1}H NMR spectrum, however, shows equally distributed charges in the three quinolinium rings, which corresponds to the charge distribution as in structure **II**.

The second example is a squaraine dye.[16] By implementation of the [4]radialene core, marked in red, the charges are in *conjugation*, because common sites for either charge exist in the canonical formulae which include electron sextet structures with internal octet stabilization.[9] The delocalization of the positive and negative charges is visualized separately (encircled in blue and red, respectively). This concept is well reflected in the fact that the NMR spectra show a symmetric molecule with equally distributed charges over the entire π-electron system. Additionally, identical bond lengths support this theory of *conjugation*.[17]



Scheme 4. Some examples of double-charged dyes; the [3]dendralene and [4]radialene cores as examples of cross-conjugated partial structures, respectively, are marked in red.

Recently, we reported on the synthesis and properties of bis-quinolines and their dicationic salts (Scheme 5), in which a 1,4-diethynyl benzene was used as a conjugated all-carbon and rigid spacer.[18]

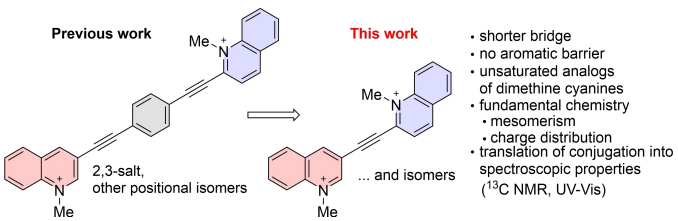
The quinolinium salts can be regarded as parent structures of double-charged cyanine dyes. However, for a more comprehensive investigation, as well as in continuation of our interest in different types of conjugation in mesomeric betaines[19] and (poly)cations,[20] we decided to examine ethynyl bridged bis-quinolinium salts, which help us to better understand the charge distribution as well as to show how it reflects in the properties of the compounds obtained.

Results and Discussion

Neutral ethynyl-bridged bisquinolines

For the synthesis of diquinoline ethynyls under Sonogashira-Hagihara conditions different approaches were used (Scheme 6). In analogy to the previously reported syntheses of 3,4-(**3b**) and 3,3-ethynyl interconnected quinolines (**3c**),[21] the 2,3-corresponding isomer **3a** was obtained in 38% yield starting from 3-ethynylquinoline **2b** (accessible in two steps[22]) and 2-chloroquinoline **1a**. In analogy to the compounds **3a**–**c**, the 2,4-interconnected isomer **3f** was formed in the reaction of 4-bromoquinoline **1c** and 2-ethynylquinoline **2a** in 20% yield, whereas the reverse reaction of 4-ethynylquinoline **2c** with the chloro derivative **1a** gave compound **3f** only in 7% yield.

Considering the symmetry of 2,2- and 4,4-interconnected quinolines (**3d**, **3e**), they were accessible in a one-pot two-fold-Sonogashira cross-coupling using an excess of the corresponding haloquinolines **1a** and **1c** for the reaction with propiolic acid. To improve the yields of the cross-coupling reactions, the amount of palladium catalyst was increased from 1 to 6-mol-% and for copper(I) iodide from 2 to 9 mol-% for both reactions. As result, the yield for **3d** was increased from 7 to 27% and for **3e** from 22 to 33%. In all cases, better yields were observed when brominated quinolines were used. The structure of **3e** was proven by X-ray structure analysis (cf. Supporting Information). Coupling phenylacetylene with halogenated quinolines resulted in almost quantitative yields in all three cases.[21]



Scheme 5. Goals of this study.

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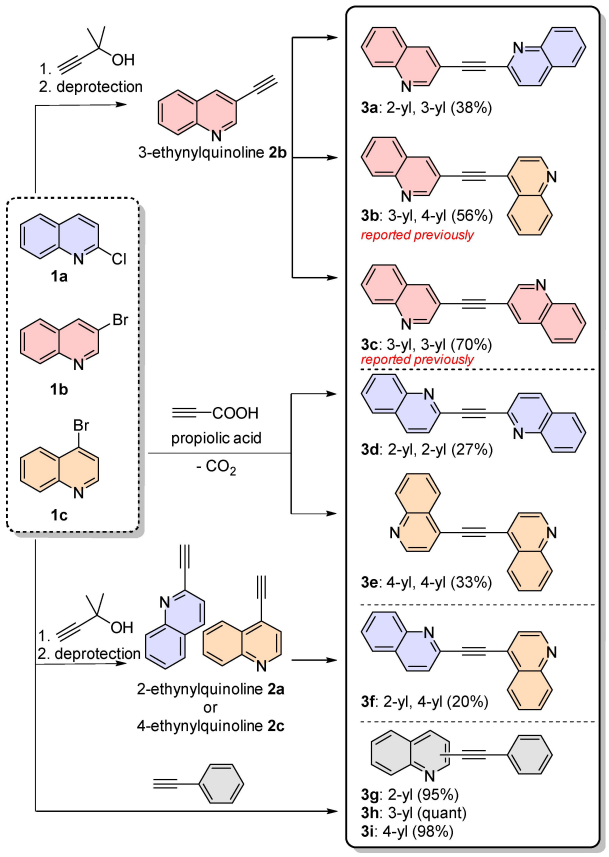
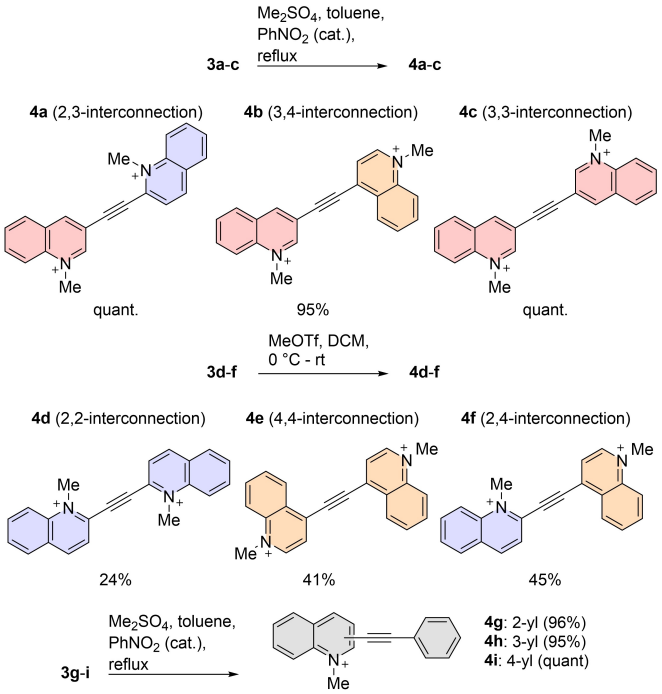


Scheme 6. Synthesis of ethynyl bridged diaromatics (**3a–i**). Conditions: $Pd(PPh_3)_2Cl_2$, CuI, NEt_3 (abs), N_2, reflux.



Scheme 7. Synthesis of quinolinium salts **4a–i**.

Syntheses of ethynyl-bridged quinolinium salts

The salts **4a–c** were formed in almost quantitative yields by reaction with an excess of dimethyl sulfate and catalytic amounts of nitrobenzene under reflux conditions in toluene (Scheme 7). In all cases, the product precipitated during the reaction and was separated by filtration and washed with ethyl acetate. Moreover, no monocationic products are observed. The same methylation procedure resulted to be reliable for the preparation of monocationic 2-, 3-, and 4-substituted quinolinium dimethylsulfates **4g–i** in quantitative yields.

However, applying the same conditions for the methylation of the symmetric 4,4-diquinoline ethynyl **3e** resulted in an incomplete conversion to the dicationic salt **4e**, as the monocationic salt is present in the crude mixture. Increasing the reaction time and the amount of dimethyl sulfate did not change the result of the reaction. Using other methylation agents such as iodomethane or Meerwein's salt also resulted in incomplete conversions. We reported previously, that the application of methyl triflate in DCM for the methylation of 1,2-di(pyridin-4-yl)ethyne resulted in the formation of a dicationic product in 56% yields.[23] Indeed, methyl triflate in DCM followed by recrystallization from methanol-ethyl ethanoate mixtures finally gave the salt **4e** in 41% yield. The quinolinium salts **4d** and **4f** were obtained analogously in 24% and 45% yields, respectively. Given the mesomeric structures, the low yields of the syntheses of the dicationic salts **4d–f** seem reasonable, as the mesomeric structure of a nitrenium ion of the monomethylated salt can be formulated according to the rules of resonance, indicating a strongly decreased nucleophilicity at this position (Scheme 8, **A**). It is a piece of evidence of how effectively the positive charge is delocalized on the entire π-electronic system in the case of 2- and 4-connections. We observed a similar chemical effect when we tried to saponify the 2-yl quinolinium salt (Scheme 8, **B**) and obtained the product of the nucleophilic addition to the C–C=C–C bond which is a site for the positive charge in one of the canonical formulae. By contrast, this is not the case for the 3-yl salt, the saponification of which proceeded very smoothly.[24] It also explains the high yields of double methylations of bis-quinolines connected via a longer π-electron system[18] (Scheme 8, **C**). Likely, the positive charge delocalization has a smaller impact on the formation of a nitrenium ion, as it is delocalized on more atoms, and the aromatic ring in between alkyne bridges serves as an additional barrier for the delocalization. In addition to that, the quaternization of analogous 1,2-di(quinolin-4-yl)ethene also was reported with low yields.[25]

Calculations and characteristic features

The 2,2-, 2,3- and 3,3-interconnected bisquinolines and their corresponding salts were chosen for geometry optimization *in vacuo* as well as in DMSO as polar solvent (6-31G*/PBE0). In all cases, the compounds are planar, or almost planar (3,3-salt **4c**) with a *transoid* conformation of the nitrogen atoms (Figure 1,

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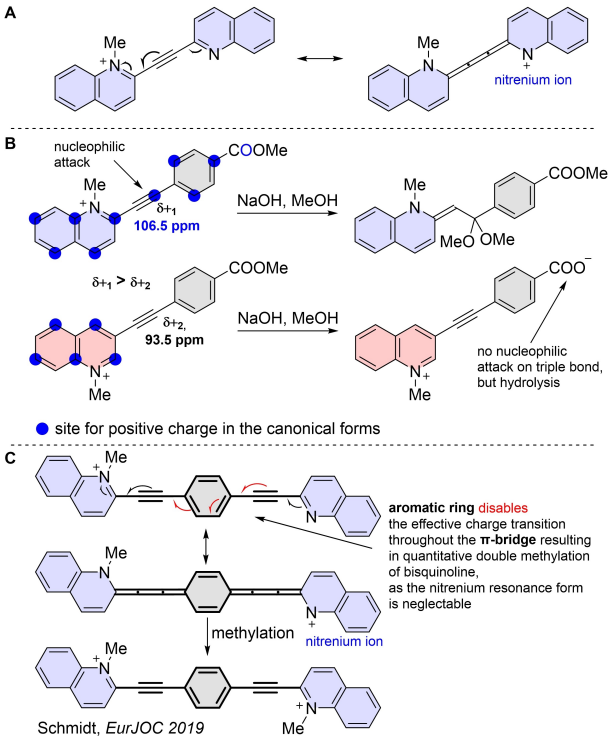

Scheme 8. Influence of positive charge delocalization on reaction outcome in different π-electronic systems.

A). The bond lengths of the salts in DMSO (in red) differ most likely due to small contributions of cumulene-type resonance structures in the case of the C2 connection when a charge is delocalized in the entire molecule. The calculated HOMO-LUMO topologies for the neutral compounds are similar in the three isomers (cf. Supporting Information). Both orbitals consist of atomic orbital coefficients which are distributed over the entire molecules. The bandgaps were calculated to be 4.17–4.23 eV. The HOMOs of the calculated salts are comparable (cf. Supporting Information). However, the LUMOs differ in all the cases and nicely reflect the mesomeric structures, where two charges are delocalized (Figure 1, **A**). The bandgaps are smaller in comparison to their neutral precursors with estimated values between 3.79 eV and 4.01 eV.

The considerable difference between the doubly charged salts is reflected in the ^{13}C NMR chemical shifts which indicate the different delocalization patterns of the charges in the resonance forms. NMR experiments were carried out in [D_6]DMSO as solvent. In the case of 3,3-interconnection (**4c**), both charges are in cross-conjugation to the attached –C≡C– bridge and localized exclusively on the quinolinium core (5 carbon atoms and the nitrogen atoms). The highest impact of a positive charge is on the carbon atoms in positions 2 and 4 of the quinoline core (152.1 and 148.9 ppm, respectively). The fused benzene ring of the quinolinium is less affected (137.9, 136.8, and 130.7 ppm for C8a, C7, and C5 atoms, respectively). The quinoline core's chemical shifts of the π-extended 3,3-salt **4c$_{extd}$** are comparable (Figure 1, **B**), as its charges are also delocalized on the same number of atoms. The calculated bond lengths (6-

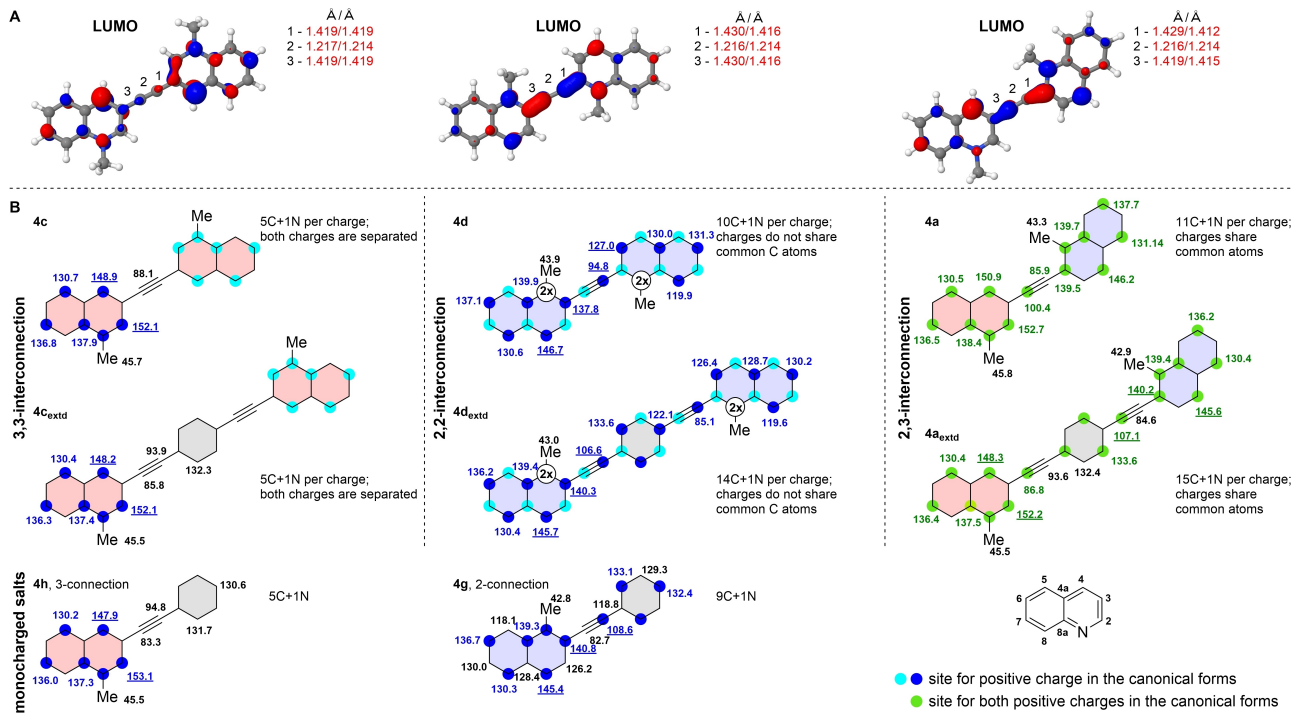

Figure 1. A. LUMO topologies of chosen ethynyl bridged bis-quinoliniums (**4c,d,a**); calculated bond lengths (in red) neutral/charged compounds, in Å; **B**. corresponding distributions of charges according to mesomeric structures of the chosen salts; characteristic ^{13}C NMR chemical shifts, marked in the same color as the assigned atom.

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31G*/PBE0) of the acetylenic spacer do not change on conversion of the neutral precursor molecule **3c** (C_{sp}^2–C_{sp}–C_{sp}–C_{sp}^2 = 1.419; 1.217; 1.419 Å) into their charged derivative **4c** (1.419; 1.214; 1.419 Å). The formal single bonds are almost identical to reference bond lengths (vinylacetylene: 1.42 Å *in vacuo* and DMSO), and the triple bond is slightly longer (acetylene: 1.20 Å *in vacuo*; 1.21 Å in DMSO).

The next examples possessing 2,2-interconnections are more complex. For a better comparison, the characteristic chemical shifts of 2- and 3-monocationic salts are also given in Figure 1. For the 2,2-interconnected salts (**4d**, $\mathbf{4d_{extd}}$), both positive charges are in conjugation over the entire π-system, however, they do not share common sites according to the rules of resonance. As a consequence, the ^{13}C NMR resonance frequencies of **4d** especially of the triple bond are considerably deshielded (94.8 ppm) in comparison to those of the 3,3-interconnected, cross-conjugated **4c** (88.1 ppm), and the same effect can be seen on comparison of the C_β's signals of the C–C≡C–C group of $\mathbf{4d_{extd}}$ (106.6 ppm) and $\mathbf{4c_{extd}}$ (93.9 ppm). As the ^{13}C NMR chemical shift of C_β of $\mathbf{4d_{extd}}$ resemble the shift of the monocationic salt **4g** (106.6 and 108.6 ppm, resp.), a similar barrier function of the central phenyl ring – as discussed in Scheme 8 – can be derived from this, because the second positive charge obviously does not affect this position considerably. This is in line with the observation that C_β of **4d** is more shielded (94.8 ppm) in comparison to C_β of $\mathbf{4d_{extd}}$ (106.6 ppm), although the overall π-electron system consists of more atoms in conjugation. However, the second positive charge takes influence on C_α of the triple bond, as expected, which shifts from 82.7 ppm (**4g**) to 85.1 ppm ($\mathbf{4d_{extd}}$). The charge distribution in the resonance forms shows parallels to the LUMO profile of the extended analog.[18] Considerable atomic orbital coefficients of the LUMO of **4d** are located on C2, C4, and the triple bond's carbon atoms. These atoms are the most affected in ^{13}C NMR spectroscopy. The calculated bond lengths of the neutral precursor molecule **3d** and its dicationic derivative **4d** differ significantly. Thus, on dication formation the C_{sp}^2– C_{sp} bond shortens from 1.430 Å (**3d**) to 1.416 Å (**4d**).

The last case (2,3-interconnection, **4a**) is a combination of the two previous cases, which results in new spectroscopic properties. Originally, one of the two charges has to be delocalized on one quinoline ring, as in **4h**, whereas the other one has to be delocalized over the entire π-system, for which **4g** is a model compound. However, according to the mesomeric structures, such a combination of two charges results in a distribution of both charges over the entire π-electron system (11 common carbon atoms and 2 nitrogen atoms). The most characteristic ^{13}C NMR peak is the C–C≡C–C triple bond carbon, which once again plays the role of a ^{13}C NMR spectroscopic indicator for the different types of conjugation and of their extensions. The carbon atom of the triple bond, which is in conjugation with the quinolinium ring, displays a signal at 100.4 ppm, indicating that the two positive charges are better delocalized than in its extended analog $\mathbf{4a_{extd}}$ (107.1 ppm), and make a higher impact, as in the 2,2-interconnected species **4d** (94.8 ppm), in which only one charge per carbon atom can be formulated. In the LUMO, a considerable atomic orbital coefficient is located on this atom. Concerning the calculated bond lengths, the behavior is a combination of the 3,3- and 2,2-interconnected species discussed before. On dication formation, the C_{sp}^2–C_{sp} bond in conjugation shortens significantly, whereas the corresponding bond in cross-conjugation is not affected (values presented in Figure 1, **A**).

Next, we turned our interest to the consequences of the different types of conjugation on the UV-Vis spectra. The spectra of the neutral compounds **3a-f** were measured in acetonitrile and methanol, respectively.

The spectral behavior of these compounds does not differ significantly. All compounds absorb light with their maximum peaks in the range from 346 to 350 nm with a small exception of 355 nm for 4,4-compound **4e**. For the extended analogs,[18] the 2,2-, 3,3-, and 2,3-interconnected bis-quinolines have a comparable π-skeleton and gave the same maximum absorption at 360 nm in acetonitrile (Figure 2), whereas the maxima of the 3,4- and 4,4-interconnected compounds were located at 364 and 366 nm, respectively.

The picture is different when we discuss the spectra of the charged analogs **4a–i**. For a better illustration, Figure 3 shows the comparison of the absorption maxima of the herein-discussed compounds with our previously reported quinolinium salts.

The propeller-shaped quinolinium and bis-quinolinium salts give no maxima with wavelength higher than 360 nm. This is caused by their shape, which restricts delocalization of the charges to the quinolinium ring.[21]

Among the quinolinium monocationic salts **4g–i**, the 3-connected, cross-conjugated **4h** has its absorption maximum at 360 nm, and the 4- and 2-connected conjugated compounds **4i**, **4g** at 371 and 376 nm, respectively. The short charged dications **4a–f** do not follow the same pattern as their π-extended derivatives. Nevertheless, the ^{13}C NMR chemical behavior of these compounds and their charge distributions in the canonical formulae is mirrored in a way in their UV-Vis spectroscopic properties. Among the conjugated systems which delocalize their two charges in the entire π-electron system, the 2,4- (**4f**) and 4,4- (**4e**) salts give their maxima at 367 and

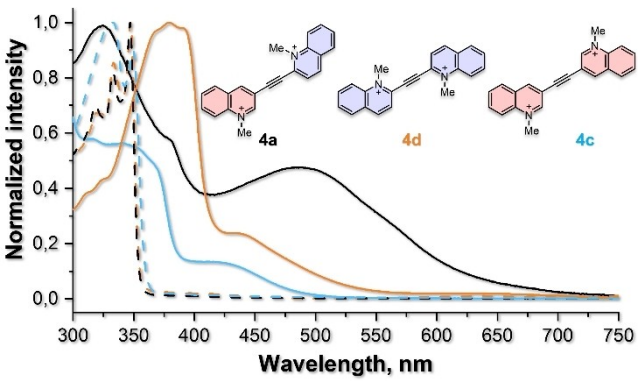

Figure 2. Chosen examples of UV-Vis spectra of salts **4a,c,d** (solid lines) as well as of their neutral precursors **3a,c,d** (dashed lines) in acetonitrile.

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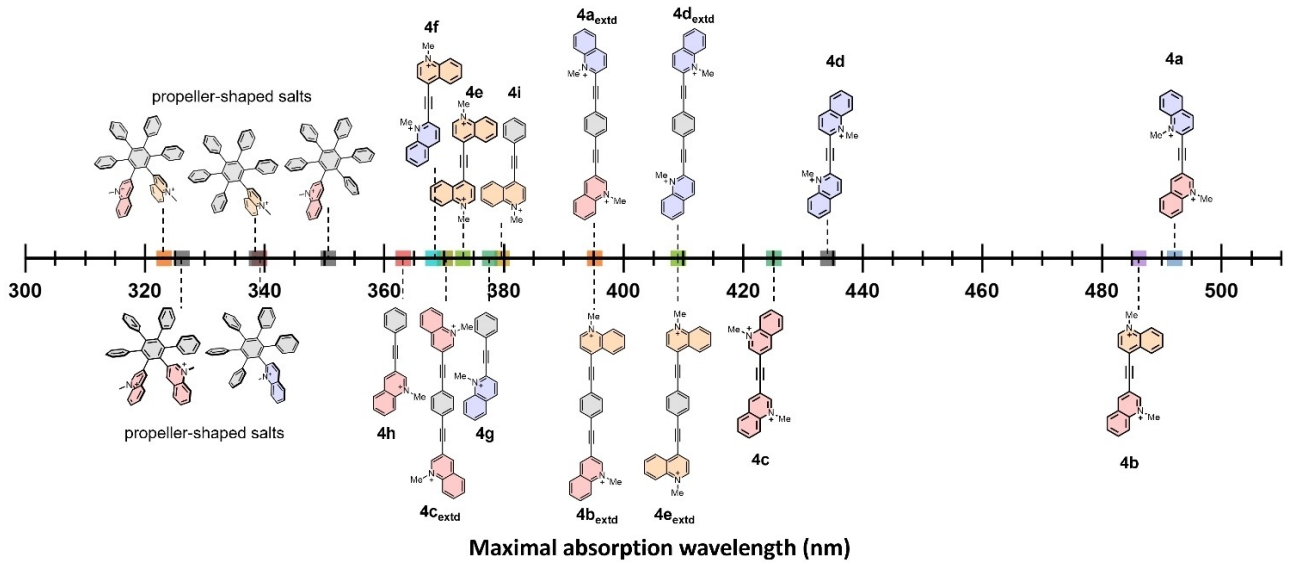

Figure 3. Comparison of UV-Vis maximal absorption wavelengths of selected quinolinium salts.

372 nm, respectively, whereas the 2,2-compound **4 d** is reaching the value of 433 nm. The cross-conjugated 3,3-interconnected salt **4 c** has its absorption maximum at 424 nm, which is 55 nm higher than the π-extended relative. Finally, the highest values have been measured for the mixed cross-conjugated/conjugated 2,3- and 3,4-salts **4 a**,**b**, the absorption maxima of which occur at 491 and 485 nm, respectively. These values exhibit bathochromic shifts of around 100 nm in comparison to the π-extended ones.

To further analyze the UV/VIS spectra, time-dependent (TD)-DFT calculations (6-31G*/PBE0) of the neutral compounds **3 a,c,d** and their corresponding dicationic salts **4 a,c,d** were performed. In all cases, the longest wavelength absorption of the cationic species is assigned to an intense ($f > 0.6$) HOMO-LUMO excitation, closely followed by HOMO-1/HOMO-2//LUMO/LUMO + 1 transitions (see Supporting Information for details, p. 66). In case of the non-symmetric salt **4 a**, the calculations revealed a significant charge-transfer (CT) from the 2-connected quinolinium to the 3-connected quinolinium residue (see the Supporting Information, p. 66). 72% of the HOMO is localized at the 2-connected quinolinium moiety (3-connected quinolinium: 19%) of which the electron density is shifted to the 3-quinolinium ring system (53% of the LUMO is located at the 3-quinolinium, 35% at the 2-quinolinium residue). This CT excitation might also explain the bathochromic shift of the non-symmetric substituted bisquinolinium salt in comparison to the symmetric derivatives in the polar solvent.

Conclusion

We present a detailed study of dicationic bis-quinolinium salts, the heteroaromatics of which are separated by acetylenic spacers. We varied the type of conjugation by preparation of cross-conjugated 3,3- and conjugated 2,2-interconnections as well as a mixed 2,3-interconnected species. For comparison, we also synthesized π-extended 1,4-diethynylbenzene spacers between the quinoliniums. The charge distribution according to the rules of resonance differs considerably in dependence on the type of conjugation. Whereas cross-conjugation results in restricted delocalizations of the positive charges in separate parts of the common π-electron system, conjugated 2,2-interconnections result in alternating, but no common sites for the positive charge delocalization. Combining either type of conjugation by 2,3-interconnection, formally dicationic atoms for the delocalization of the positive charges exist. These formalisms translate into ^{13}C NMR as well as UV-Vis-spectroscopic properties which also correlate with the calculated LUMO geometries of the molecules. We found that the triple bond's resonance frequencies can serve as ^{13}C NMR spectroscopic indicators for the type of conjugation, as these react sensitive toward any changes and combinations of differently conjugated partial structures. It is known that implementing a positive charge into a neutral molecule results in a change of the absorbance to longer wavelengths, and the more atoms involved in delocalization, the stronger the shift. We show here that for the case of two positive charges, the type of conjugation and their combination translates significantly into the UV-Vis spectroscopic behavior. Thus, the combination of cross-conjugation with conjugated structure elements of dicationic dyes results in considerable bathochromic shifts. Following the same logic as for monocationic salts and considering the UV/VIS data and the characteristic NMR shifts, we can conclude, that two positive charges are best delocalized when they share the same atoms in their resonance forms. This is, however, only then realized, when no barrier caused by inappropriate geometries of the molecule or aromatic stabilization is realized between two charges. This paper therefore contributes to a deeper understanding of the phenomenon of conjugation and the relationship between classical resonance forms, LUMO profiles, and physical properties.

Experimental Section

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}. ^1H NMR spectra were recorded at 400 MHz or 600 MHz. ^{13}C NMR spectra were recorded at 100 MHz or 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 electrospray ionization mass spectra (ESIMS) were measured with a Bruker Impact-II mass spectrometer. Samples were sprayed from MeCN. Chromatography: The reactions were traced by thin layer chromatography with silica gel 60 (F254, 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).

Calculation: All density-functional theory (DFT)-calculations were carried out by using the multithreaded Firefly 8.2.0 QC package,[26] which is partially based on the GAMESS (US)[27] source code, running on Windows 10 Pro (Version 10.0.17763.914) (x86_64) on an 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. 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.[28] Compositions of molecular orbitals were calculated using the AOMix program.[29]

Crystal Structure Determinations of 3 e: The single-crystal X-ray diffraction studies was carried out on a Bruker D8 Venture diffractometer with PhotonII detector at 123(2) K using Cu–Kα radiation (λ = 1.54178 Å). Dual space Methods (SHELXT)[30] were used for structure solution and refinement was carried out using SHELXL-2014 (full-matrix least-squares on F^2). Hydrogen atoms were localized by difference electron density determination and refined using a riding model. A semi-empirical absorption correction was applied.

3 e: pale yellow crystals, $C_{20}H_{12}N_2$, M_r = 280.32, crystal size 0.16 × 0.12 × 0.06 mm, monoclinic, space group $P2_1/c$ (no. 14), a = 6.9699(2) Å, b = 10.6843(3) Å, c = 9.2192(3) Å, β = 96.090(1)°, V = 682.67(4) $Å^3$, Z = 2, ρ = 1.364 Mg/m^{-3}, μ(Cu-K_α) = 0.63 mm^{-1}, F(000) = 292, $2\theta_{max}$ = 144.4°, T = 123 K, 7686 reflections, of which 1335 were independent (R_{int} = 0.024), 100 parameters, R_1 = 0.033 (for 1311 $I > 2\sigma(I)$), wR_2 = 0.092 (all data), S = 1.08, largest diff. peak/hole = 0.22/−0.15 e $Å^{-3}$.

Deposition Number(s) 2212119 (**3 e**) contains the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

2-Methyl-4-(quinolin-3-yl)but-3-in-2-ol[31] and compounds **2 b**,[31] **3 b**,**c**,**g**–**i**, [21] **4 h**[32] were synthesised as reported in our previous papers. Some parts of Experimental Section are taken from a dissertation.[33]

General Procedure of the Sonogashira-Hagihara Coupling (Procedure 1): The reactions were carried out under a nitrogen atmosphere. A mixture of 5 mmol of the aryl halides, 1 mol-% of $Pd(PPh_3)_2Cl_2$, and 2 mol-% of CuI was suspended in 7 mL of anhydrous NEt_3 with stirring. A sample of the corresponding ethyne (1.05 equiv.) in dry NEt_3 was added dropwise at ambient temperature. The resulting solutions were then stirred at reflux temperature until complete conversion was monitored by TLC. The mixtures were then cooled to r.t. and the solvents were removed *in vacuo*. The resulting residues were finally purified by column chromatography (petroleum ether/ethyl acetate) to afford the products.

2-Methyl-4-(quinolin-2-yl)but-3-yn-2-ol: According to the Procedure 1, a solution of 0.820 g (5.00 mmol) of 2-chloroquinoline **1 a**, 0.020 g (0.01 mmol) of CuI, 0.040 g (0.05 mmol) of $Pd(PPh_3)_2Cl_2$, and 0.51 mL (5.25 mmol) of MEBYNOL in 12 mL of anhydrous NEt_3 were reacted for 1.5 h. Finally, a purification by column chromatography (petroleum ether/ethyl acetate = 2 : 1) gave 2-methyl-4-(quinolin-2-yl)but-3-yn-2-ol. Yield 0.978 g, 92 %, a light-yellow solid, m.p. 105–106 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.11 (d, J = 8.3 Hz, 1H), 8.10 (d, J = 8.6 Hz, 1H), 7.79 (dd, J = 1.3, 8.1 Hz, 1H), 7.74–7.70 (m, 1H), 7.56–7.52 (m, 1H), 7.49 (d, J = 8.6 Hz, 1H), 2.42 (br.s, 1H), 1.69 (s, 6H) ppm. Spectroscopic data are in agreement with those reported in the literature.[34]

2-Methyl-4-(quinolin-4-yl)but-3-in-2-ol: According to the Procedure 1, a solution of 1.040 g (5.00 mmol) of 4-bromoquinoline **1 c**, 0.020 g (0.01 mmol) of CuI, 0.040 g (0.05 mmol) of $Pd(PPh_3)_2Cl_2$, and 0.51 mL (5.25 mmol) of MEBYNOL in 12 mL of anhydrous NEt_3 were reacted for 2 h. Finally, a purification by column chromatography (petroleum ether/ethyl acetate = 2 : 1) gave 2-methyl-4-(quinolin-4-yl)but-3-in-2-ol. Yield 0.966 g, 91 %, an orange solid, m.p. 97–98 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.86 (d, J = 4.5 Hz, 1H, 2-H), 8.20 (dd, J = 1.3, 8.3, 1H, 5-H), 8.12 (d, J = 8.3 Hz, 1H, 8-H), 7.75–7.71 (m, 1H, 7-H), 7.62–7.57 (m, 1H, 6-H), 7.44 (d, J = 4.5 Hz, 1H, 3-H), 2.56 (br. s, 1H, O*H*), 1.74 (s, 6H, 2CH_3) ppm. Spectroscopic data are in agreement with those reported in the literature.[35]

General Procedure of Synthesis of the Terminal Alkynes (Procedure 2): The reactions were carried out under a nitrogen atmosphere. A flask was charged with the protected acetylenes (1.00 mmol), KOH (1.05 mmol), K_3PO_4 (1.05 mmol), and anhydrous toluene (40 mL). Then the flask was immersed in a preheated oil bath (200 °C). The suspensions were stirred vigorously under reflux temperature until complete conversion, as monitored by TLC. The mixtures were then cooled to r.t. After evaporation of the organic phase to dryness, the resulting residues were finally purified by column chromatography (petroleum ether/ethyl acetate) to afford the products.

2-Ethynylquinoline (2 a): According to Procedure 2, a solution of 0.400 g (1.89 mmol) of 2-methyl-4-(quinolin-2-yl)but-3-yn-2-ol, 0.112 g (2.00 mmol) of KOH, and 0.422 g (2.00 mmol) of K_3PO_4 in 20 mL of anhydrous toluene was heated (3 min) under reflux temperature. Finally, a purification by column chromatography (petroleum ether/ethyl acetate = 3 : 1) gave 2-ethynylquinoline **2 a**. Yield 0.158 g, 55 %, a yellow solid. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.14 (d, J = 8.5 Hz, 1H), 8.11 (d, J = 8.6 Hz, 1H),7.81 (dd, J = 1.1, 7.9 Hz, 1H), 7.76-7.71 (m, 1H), 7.58–7.54 (m, 1H), 7.55 (d, J = 8.6 Hz, 1H), 3.25 (s, 1H) ppm. Spectroscopic data are in agreement with those reported in the literature.[34]

4-Ethynylquinoline (2 c): According to Procedure 2, a solution of 0.300 g (1.42 mmol) of 2-methyl-4-(quinolin-4-yl)but-3-yn-2-ol, 0.084 g (1.49 mmol) of KOH and 0.316 g (1.49 mmol) of K_3PO_4 in 20 mL of anhydrous toluene was heated (10 min) under reflux temperature. Finally, a purification by column chromatography (petroleum ether/ethyl acetate = 1.5 : 1) gave 4-ethynylquinoline **2 c**. Yield 0.165 g, 75 %, a white solid, m.p. 103-104 °C. ^1H NMR

(400 MHz, $CDCl_3$): $\delta = 8.88$ (d, $J = 4.4$ Hz, 1H, 2-H), 8.28 (dd, $J = 0.8$, 8.3 Hz, 1H, 5-H), 8.12 (d, $J = 8.1$ Hz, 1H, 8-H), 7.77–7.73 (m, 1H, 7-H), 7.64–7.60 (m, 1H, 6-H), 7.54 (d, $J = 4.4$ Hz, 1H, 3-H), 3.66 (s, 1H, CC*H*) ppm. Spectroscopic data are in agreement with those reported in the literature.**2-((Quinolin-3-yl)ethynyl)quinoline (3a)**: According to Procedure **1a** solution of 0.163 g (1.00 mmol) of 2-chloroquinoline **1a**, 0.070 g (0.10 mmol) of $Pd(PPh_3)_2Cl_2$, 0.038 g (0.20 mmol) of CuI, and 0.218 g (1.05 mmol) of 3-ethynylquinoline **2b** in 10 mL of anhydrous NEt_3 was heated (3.5 h) under reflux temperature. Finally, a purification by column chromatography (petroleum ether:ethyl acetate = 3:1) gave 2-((quinolin-3-yl)ethynyl)quinoline **3a**. Yield 0.107 g, 38%, an orange solid, m.p. 137–138 °C (decomp.). ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 9.11$ (d, $J = 1.8$ Hz, 1H, 2-H), 8.44 (s, 1H, 4-H), 8.16 (d, $J = 8.5$ Hz, 1H, 4′-H), 8.14 (d, $J = 8.5$ Hz, 1H, 8′-H), 8.11 (d, $J = 8.5$ Hz, 1H, 8-H), 7.82–7.80 (m, 2H, 5-H, 5′-H), 7.76–7.73 (m, 2H, 7-H, 7′-H), 7.65 (d, $J = 8.5$ Hz, 1H, 3′-H), 7.59–7.55 (m, 2H, 6-H, 6′-H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 152.2$ (+, C2), 148.4 (o, C8a′), 147.3 (o, C8a), 143.1 (o, C2′), 139.6 (+, C4), 136.5 (+, C4′), 130.7 (+, C7), 130.4 (+, C7′), 129.6 (+, C8), 129.5 (+, C8′), 127.9 (+, C5), 127.7 (+, C5′), 127.6 (+, C6), 127.5 (+, C6′), 127.4 (o, C4a), 127.2 (o, C4a′), 124.4 (+, C3′), 116.4 (o, C3), 92.4 (o, Cβ), 87.0 (o, Cα) ppm. IR (ATR): 2923, 2218, 2208, 1589, 1552, 1488, 1422, 1350, 1309, 1239, 1124, 1104, 1015, 985, 955, 908, 824, 786, 747, 635, 593, 551, 499, 470 cm^{-1}. HRMS (ESI): *m/z* calcd. for $C_{20}H_{13}N_2$ $[M+H]^+$ 281.1074, found 281.1080.

2,2′-(Ethyne-1,2-diyl)diquinoline (3d): A solution of 0.410 g (2.50 mmol) of 2-chloroquinoline **1a**, 0.040 g (0.06 mmol) of $Pd(PPh_3)_2Cl_2$, and 0.020 g (0.10 mmol) of CuI in 15 mL of anhydrous NEt_3 was cooled down to 0 °C. Then 0.07 mL (1.05 mmol) of propiolic acid was added dropwise. The formed mixture was heated (3 h) under reflux temperature. Finally, a purification by column chromatography (petroleum ether:ethyl acetate = 4:1) gave 2,2′-(ythyne-1,2-diyl)diquinoline **3d**. Yield 0.080 g, 27%, a brownish solid, m.p. 172–173 °C. ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 8.19$ (d, $J = 8.4$ Hz, 2H, 4-H, 4′-H), 8.16 (d, $J = 8.5$ Hz, 2H, 8-H, 8′-H), 7.83 (d, $J = 8.1$ Hz, 2H, 5-H, 5′-H), 7.77 (d, $J = 8.4$ Hz, 2H, 3-H, 3′-H), 7.76 (ddd, $J = 1.5$, 6.7, 8.6 Hz, 2H, 7-H, 7′-H), 7.59–7.57 (m, 2H, 6-H, 6′-H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 148.4$ (o, C8a, C8a′), 142.9 (o, C2, C2′), 136.5 (+, C4, C4′), 130.3 (+, C7, C7′), 129.6 (+, C8, C8′), 127.72 (+, C6, C6′), 127.67 (+, C5, C5′), 127.6 (o, C4a, C4a′), 124.8 (+, C3, C3′), 89.0 (o, Cα, Cβ) ppm. IR (ATR): 3054, 2955, 2922, 2853, 1728, 1589, 1549, 1498, 1422, 1288, 1117, 824, 790, 754, 621, 480 cm^{-1}. HRMS (ESI): *m/z* calcd. for $C_{20}H_{12}N_2Na$ $[M+Na]^+$ 303.0893, found 303.0895.

4,4′-(Ethyne-1,2-diyl)diquinoline (3e): A solution of 0.416 g (2.00 mmol) of 4-bromoquinoline **1c**, 0.040 g (0.06 mmol) of $Pd(PPh_3)_2Cl_2$, and 0.017 g (0.09 mmol) of CuI in 13 mL of anhydrous NEt_3 was cooled down to 0 °C. Then 0.07 mL (1.05 mmol) of propiolic acid was added dropwise and stirred overnight at r.t. Then, the formed mixture was heated (2 h) under reflux temperature. Finally, a purification by column chromatography (petroleum ether:ethyl acetate = 3:1) gave 4,4′-(ythyne-1,2-diyl)diquinoline **3e**. Yield 0.092 g, 33%, a yellow solid, m.p. 173–174 °C. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.98$ (d, $J = 4.4$ Hz, 2H, 2-H, 2′-H), 8.42 (dd, $J = 0.9$, 8.3 Hz, 2H, 5-H, 5′-H), 8.19 (d, $J = 8.3$ Hz, 2H, 8-H, 8′-H), 7.83–7.79 (m, 2H, 7-H, 7′-H), 7.72–7.68 (m, 2H, 6-H, 6′-H), 7.74 (d, $J = 4.4$ Hz, 2H, 3-H, 3′-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 149.9$ (+, C2, C2′), 148.3 (o, C8a, C8a′), 130.34 (+, C7, C7′), 130.26 (+, C8, C8′), 128.7 (o, C4, C4′), 127.9 (+, C6, C6′), 127.5 (o, C4a, C4a′), 125.9 (+, C5, C5′), 124.3 (+, C3, C3′), 93.7 (o, Cα, Cβ) ppm. IR (ATR): 2922, 2852, 1729, 1580, 1503, 1040, 846, 760, 640, 574, 539, 486, 424 cm^{-1}. HRMS (ESI): *m/z* calcd. for $C_{20}H_{13}N_2$ $[M+H]^+$ 281.1073, found 281.1080.

2-((Quinolin-4-yl)ethynyl)quinoline (3f): Route I. Similarly to Procedure 1, a solution of 0.206 g (0.99 mmol) of 4-bromoquinoline **1c**, 0.007 g (0.01 mmol) of $Pd(PPh_3)_2Cl_2$, 0.004 g (0.02 mmol) of CuI, and 0.144 g (0.95 mmol) of 2-ethynylquinoline **2a** in 15 mL of anhydrous NEt_3 was stirred overnight at r.t., and then heated for 3 h under reflux temperature. Finally, a purification by column chromatography (petroleum ether:ethyl acetate = 3:1) gave 2-((quinolin-4-yl)ethynyl)quinoline **3f**; Route II. Similarly to Procedure 1, a solution of 0.063 g (0.38 mmol) of 2-chloroquinoline **1a**, 0.015 g (0.022 mmol) of $Pd(PPh_3)_2Cl_2$, 0.006 g (0.033 mmol) of CuI, and 0.056 g (0.36 mmol) of 4-ethynylquinoline **2c** in 10 mL of anhydrous NEt_3 was heated for 3 h under reflux temperature. Finally, a purification by column chromatography (petroleum ether:ethyl acetate = 3:1) gave 2-((quinolin-4-yl)ethynyl)quinoline **3f**. Yield 0.052 g, 20%, an orange-yellow solid, (route I), or 0.040 g, 39% (route II), m.p. 110–111 °C. ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 8.94$ (d, $J = 4.3$ Hz, 1H, 2′-H), 8.46 (d, $J = 8.2$ Hz, 1H, 5′-H), 8.22 (d, $J = 8.4$ Hz, 1H, 4-H), 8.17 (d, $J = 8.6$ Hz, 1H, 8-H), 8.16 (d, $J = 8.9$ Hz, 1H, 8′-H), 7.84 (d, $J = 8.1$ Hz, 1H, 5-H), 7.79–7.76 (m, 2H, 7-H, 7′-H), 7.74 (d, $J = 8.4$ Hz, 1H, 3-H), 7.70 (d, $J = 4.3$ Hz, 1H, 3′-H), 7.68–7.66 (m, 1H, 6′-H), 7.61–7.58 (m, 1H, 6-H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 149.9$ (+, C2′), 148.5 (o, C8a), 148.2 (o, C8a′), 142.7 (o, C2), 136.6 (+, C4), 130.5 (+, C7), 130.2 (+, C7′), 130.1 (+, C8′), 129.6 (+, C8), 128.7 (o, C4′), 127.81 (+, C6), 127.77 (o, C4a′), 127.74 (+, C5), 127.63 (+, C6′), 127.58 (o, C4a), 126.2 (+, C5′), 124.6 (+, C3), 124.5 (+, C3′), 97.8 (o, Cα), 85.0 (o, Cβ) ppm. IR (ATR): 3053, 3303, 2922, 2209, 1928, 1591, 1500, 1220, 1389, 1114, 823, 751, 643, 475 cm^{-1}. HRMS (ESI): *m/z* calcd. for $C_{20}H_{12}N_2Na$ $[M+Na]^+$ 303.0893, found 303.0889.

General Procedure for the Preparation of the Salts 4a and 4g–i (Procedure 3): Samples of 0.50 mmol of the corresponding quinoline derivatives were dissolved in toluene containing 1 drop of nitrobenzene. Then an excess 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 products.

1-Methyl-3-((1-methylquinolinium-2-yl)ethynyl)quinolinium dimethylsulfate (4a): According to Procedure 3, a solution of 0.070 g (0.25 mmol) of 2-((quinolin-3-yl)ethynyl)quinoline **3a**, 1 drop of nitrobenzene and 0.12 mL (1.25 mmol) of dimethyl sulfate in 7 mL of anhydrous toluene was heated (3 h) under reflux temperature to give 1-methyl-3-((1-methylquinolin-1-ium-2-yl)ethynyl)quinolin-1-ium dimethylsulfate **4a**. Yield 0.133 g, 100%, a dark violet solid, m.p. 169-170 °C. ^{1}H NMR (600 MHz, [D_6]DMSO): $\delta = 10.16$ (s, 1H, 2-H), 9.89 (s, 1H, 4-H), 9.36 (d, $J = 8.5$ Hz, 1H, 4′-H), 8.69 (d, $J = 8.8$ Hz, 1H, 8-H), 8.64 (d, $J = 8.8$ Hz, 1H, 8′-H), 8.56 (d, $J = 7.7$ Hz, 1H, 5′-H), 8.52 (d, $J = 8.2$ Hz, 1H, 5-H), 8.50 (d, $J = 8.5$ Hz, 1H, 3′-H), 8.44 (ddd, $J = 1.5$, 7.1, 8.7 Hz, 1H, 7′-H), 8.37 (ddd, $J = 1.6$, 7.1, 8.8 Hz, 1H, 7-H), 8.19 (t, $J = 7.1$ Hz, 1H, 6′-H), 8.12 (t, $J = 7.1$ Hz, 1H, 6-H), 4.90 (s, 3H, N′CH_3), 4.72 (s, 3H, NCH_3), 3.36 (s, 6H, 2CH_3SO_4) ppm. ^{13}C NMR (150 MHz, [D_6]DMSO): $\delta =$ 152.7 (+, C2), 150.9 (+, C4), 146.2 (+, C4′), 139.7 (o, C8a′), 139.5 (o, C2′), 138.4 (o, C8a), 137.7 (+, C7′), 136.5 (+, C7), 131.14 (+, C5′), 131.13 (+, C6′), 130.54 (+, C6), 130.48 (+, C5), 129.0 (o, C4a), 128.5 (o, C4a′), 126.2 (+, C3′), 119.8 (+, C8), 119.6 (+, C8′), 113.6 (o, C3), 100.4 (o, Cα), 85.9 (o, Cβ), 52.9 (+, CH_3SO_4), 45.8 (+, NCH_3), 43.3 (+, N′CH_3) ppm. IR (ATR): 2946, 2832, 2225, 1595, 1520, 1456, 1380, 1356, 1214, 1057, 1043, 1001, 884, 836, 729, 659, 607, 575, 550, 500, 429 cm^{-1}. HRMS (ESI): *m/z* calcd. for $C_{22}H_{18}N_2$ $[M]^{2+}$ 155.0730, found 155.0736.

1-Methyl-3-((1-methylquinolinium-4-yl)ethynyl)quinolinium dimethylsulfate (4b): According to Procedure 3, a solution of 0.070 g (0.25 mmol) of 3-(quinolin-4-ylethynyl)quinoline **3b**, 1 drop of nitrobenzene and 0.12 mL (1.25 mmol) of dimethyl sulfate in 7 mL of anhydrous toluene was heated (3 h) under reflux temperature to give 1-methyl-3-((1-methylquinolinium-4-yl)ethynyl)quinolinium dimethylsulfate **4b**. Yield 0.126 g, 95%, a khaki-colored solid, m.p.

223–224 °C. ^{1}H NMR (600 MHz, [D$_6$]DMSO): δ = 10.16 (d, J = 0.9 Hz, 1H, 2-H), 9.86 (s, 1H, 4-H), 9.60 (d, J = 6.4 Hz, 1 H, 2′-H), 8.93 (dd, J = 1.0, 8.3 Hz, 5′-H), 8.63 (d, J = 8.8 Hz, 1H, 8′-H) 8.63 (d, J = 8.7 Hz, 1H, 8-H), 8.55 (d, J = 8.2 Hz, 1H, 5-H), 8.47 (d, J = 5.95 Hz, 3′-H) 8.43–8.39 (m, 2H, 7-H, 7′-H), 8.24 (ddd, J = 0.8, 7.14, 8.10 Hz, 1H, 6′-H), 8.18 (ddd, J = 0.7, 7.7, 8.0 Hz, 1H, 6-H), 4.73 (s, 3H, NCH$_3$), 4.69 (s, 3H, N′CH$_3$), 3.37 (s, 6H, 2CH$_3$SO$_4$) ppm. ^{13}C NMR (150 MHz, [D$_6$]DMSO): δ = 152.8 (+, C2), 150.3 (+, C4), 149.9 (+, C2′), 138.5 (o, C8a′), 138.1 (o, C8a), 137.3 (+, C7), 136.6 (o, C4′), 136.0 (+, C7′), 131.1 (+, C6′), 131.0 (+, C6), 130.9 (+, C5), 128.6 (o, C4a), 128.4 (o, C4a′), 127.8 (+, C5′), 125.0 (+, C3′), 120.1 (+, C8′), 119.6 (+, C8), 114.6 (o, C3), 99.1 (o, Cα), 87.9 (o, Cβ), 52.8 (+, 2CH$_3$SO$_4$), 45.7 (+, NCH$_3$), 45.7 (+, N′CH$_3$) ppm. IR (ATR): 3040, 2219, 1604, 1527, 1435, 1402, 1371, 1331, 1222, 1143, 1058, 1003, 857, 770, 726, 702, 609, 577, 552, 507, 447, 429 cm^{-1}. HRMS (ESI): *m/z* calcd. for $C_{22}H_{18}N_2$ [M]$^{2+}$ 155.0730, found 155.0740.

3,3′-Ethyne-1,2-diylbis(1-methylquinolinium) dimethylsulfate (4c): According to Procedure 3, a solution of 0.070 g (0.25 mmol) of 3,3′-ethyne-1,2-diyldiquinoline **3c**, 1 drop of nitrobenzene and 0.12 mL (1.25 mmol) of dimethyl sulfate in 7 mL of anhydrous toluene was heated (3 h) under reflux temperature to give 3,3′-ethyne-1,2-diylbis(1-methylquinolinium) dimethylsulfate **4c**. Yield 0.133 g, 100 %, a bone-colored solid, m.p. 234-235 °C (decomp.). ^{1}H NMR (600 MHz, [D$_6$]DMSO): δ = 9.94 (d, J = 1 Hz, 2H, 2-H, 2′-H), 9.60 (s, 2H, 4-H, 4′-H), 8.60 (d, J = 8.8 Hz, 2H, 8-H, 8′-H), 8.54 (d, J = 8.3 Hz, 2H, 5-H, 5′-H), 8.38 (ddd, J = 1.5, 7.1, 8.6 Hz, 2H, 7-H, 7′-H), 8.16 (t, J = 7.7 Hz, 2H, 6-H, 6′-H), 4.70 (s, 6H, NCH$_3$, N′CH$_3$), 3.37 (s, 6H, 2CH$_3$SO$_4$) ppm. ^{13}C NMR (150 MHz, [D$_6$]DMSO): δ = 152.1 (+, C2, C2′), 148.9 (+, C4, C4′), 137.9 (o, C8a, C8a′), 136.8 (+, C7, C7′), 130.9 (+, C6, C6′), 130.7 (+, C5, C5′), 128.7 (o, C4a, C4a′), 119.4 (+, C8, C8′), 115.2 (o, C3, C3′), 88.1 (o, Cα, Cβ), 52.9 (+, 2CH$_3$SO$_4$), 45.7 (+, NCH$_3$, N′CH$_3$) ppm. IR (ATR): 3043, 2945, 1610, 1577, 1520, 1442, 1381, 1351, 1215, 1140, 1054, 1002, 873, 771, 730, 660, 608, 577, 554, 499, 456, 430 cm^{-1}. HRMS (ESI): *m/z* calcd. for $C_{22}H_{18}N_2$ [M]$^{2+}$ 155.0730, found 155.0716.

2,2′-(Ethyne-1,2-diyl)bis(1-methylquinolinium) ditrifluormethylsulfonate (4d): A solution of 0.040 g (0,14 mmol) of 2,2′-ethyne-1,2-diyldiquinoline **3d** in dry DCM (6 mL) was cooled down to 0 °C. Then 0.230 g (1.39 mmol) of methyl triflate was added dropwise. The formed mixture was stirred for 30 h at r.t. The crude product was filtered off and recrystallized from a methanol-ethyl acetate mixture (1 : 1) to give crystals which were crushed out from a solution after 4 days at r.t. Yield 0.020 g, 24 %, a light brown colored solid, m.p. 239–240 °C (decomp.). ^{1}H NMR (600 MHz, [D$_6$]DMSO): δ = 9.48 (d, J = 8.7 Hz, 2H, 4-H, 4′-H), 8.84 (d, J = 8.7 Hz, 2H, 3-H, 3′-H), 8.74 (d, J = 9 Hz, 2H, 8-H, 8′-H), 8.56 (dd, J = 0.8, 8.1 Hz, 2H, 5-H, 5′-H), 8.44–8.42 (m, 2H, 7-H, 7′-H), 8.19–8.16 (m, 2H, 6-H, 6′-H), 4.91 (s, 6H, NC*H*$_3$, N′C*H*$_3$) ppm. ^{13}C NMR (150 MHz, [D$_6$]DMSO): δ = 146.7 (+, C4, C′4), 139.9 (o, C8a, C′8a), 137.8 (o, C2, C′2), 137.1 (+, C7, C′7), 131.3 (+, C6, C′6), 130.6 (+, C5, C′5), 130.0 (o, C4a, C′4a), 127.0 (+, C3, C′3), 119.9 (+, C8, C′8), 119.6 (o, 2CF_3SO$_3$), 94.8 (o, Cα, Cβ), 43.9 (+, NCH$_3$, N′CH$_3$) ppm. IR (ATR): 3078, 3027, 1618, 1592, 1580, 1521, 1437, 1382, 1358, 1302, 1256, 1224, 1149, 1122, 1059, 1028, 966, 884, 776, 765, 752, 701, 633, 591, 572, 515, 506, 481, 463, 406 cm^{-1}. HRMS (ESI): *m/z* calcd. for $C_{22}H_{18}N_2$ [M]$^{2+}$ 155.0730, found 155.0726.

4,4′-(Ethyne-1,2-diyl)bis(1-methylquinolinium) ditrifluormethylsulfonate (4e): A solution of 0.100 g (0,36 mmol) of 4,4′-ethyne-1,2-diyldiquinoline **3e** in dry DCM (10 mL) was cooled down to 0 °C. Then 0.590 g (3.57 mmol) of methyl triflate was added dropwise. The formed mixture was stirred for 30 h at r.t. The crude product was filtered off and recrystallized from a methanol-ethyl acetate mixture (1 : 1) to give crystals which were crushed out from a solution after 2 days at r.t. Yield 0.089 g, 41 %, light-yellow needles, m.p. 306–307 °C (decomp.). ^{1}H NMR (600 MHz, [D$_6$]DMSO): δ = 9.71 (d, J = 5.8 Hz, 2H, 2-H, 2′-H), 8.93 (d, J = 8.3 Hz, 2H, 5-H, 5′-H), 8.83 (d, J = 5.8 Hz, 2H, 3-H, 3′-H), 8.66 (d, J = 8.8 Hz, 2H, 8-H, 8′-H), 8.44–8.41 (m, 2H, 7-H, 7′-H), 8.26–8.23 (m, 2H, 6-H, 6′-H), 4.72 (s, 6H, NC*H*$_3$, N′C*H*$_3$) ppm. ^{13}C NMR (150 MHz, [D$_6$]DMSO): δ = 149.9 (+, C2, C2′), 138.5 (o, C8a, C8a′), 136.1 (+, C7, C′7), 135.7 (o, C4, C′4), 131.4 (+, C6, C′6), 128.5 (o, C4a, C4a′), 127.9 (+, C5, C′5), 126.3 (+, C3, C′3), 120.1 (+, C8, C′8), 119.6 (o, 2CF_3SO$_3$), 97.1 (o, Cα, Cβ), 45.9 (+, NCH$_3$, N′CH$_3$) ppm. IR (ATR): 3089, 1602, 1584, 1527, 1413, 1372, 1326, 1255, 1153, 1121, 1026, 857, 809, 768, 709, 635, 573, 546, 516, 464, 427 cm^{-1}. HRMS (ESI): *m/z* calcd. for $C_{22}H_{18}N_2$ [M]$^{2+}$ 155.0730, found 155.0736.

1-Methyl-4-((1-methylquinolinium-2-yl)ethynyl)quinolinium ditrifluormethylsulfonate (4f): A solution of 0.130 g (0,48 mmol) of 2-((quinolin-4-yl)ethynyl)quinoline **3f** in dry DCM (12 mL) was cooled down to 0 °C. Then 0.790 g (4.78 mmol) of methyl triflate was added dropwise. The formed mixture was stirred for 30 h at r.t. The crude product was filtered off and recrystallized from a methanol-ethyl acetate mixture (1 : 1) to give crystals which were crushed out from a solution after 2 days at r.t. Yield 0.132 g, 45 %, light-yellow needles, m.p. 275–276 °C. ^{1}H NMR (600 MHz, [D$_6$]DMSO): δ = 9.74 (d, J = 5.6 Hz, 1H, 2′-H), 9.45 (d, J = 8.4 Hz, 1H, 4-H), 8.89 (d, J = 7.9 Hz, 1H, 5′-H), 8.86 (d, J = 8.4 Hz, 1H, 3-H), 8.84 (d, J = 5.6 Hz, 1H, 3′-H), 8.74 (d, J = 9.0 Hz, 1H, 8-H), 8.68 (d, J = 8.7 Hz, 1H, 8′-H), 8.56 (dd, J = 1.0, 8.2 Hz, 1H, 5-H), 8.45–8.40 (m, 2H, 7-H, 7′-H), 8.27–8.25 (m, 1H, 6′-H), 8.17-8.15 (m, 1H, 6-H), 4.94 (s, 3H, NC*H*$_3$), 4.74 (s, 3H, N′C*H*$_3$) ppm. ^{13}C NMR (150 MHz, [D$_6$]DMSO): δ = 150.0 (+, C′2), 146.3 (+, C4), 139.7 (o, C8a), 138.8 (o, C2), 138.5 (o, C′8a), 136.8 (+, C7), 136.2 (+, C7), 134.5 (o, C′4), 131.6 (+, C′6), 131.0 (+, C6), 130.5 (+, C5), 129.5 (o, C4a), 128.5 (o, C′4a), 127.8 (+, C′5), 127.1 (+, C3), 126.6 (+, C′3), 120.1 (+, C′8), 119.8 (+, C8), 119.6 (o, 2CF_3SO$_3$), 98.0 (o, Cβ), 94.3 (o, Cα), 46.0 (+, N′CH_3), 43.7 (+, NCH_3) ppm. IR (ATR): 3093, 2286, 1977, 1615, 1597, 1580, 1523, 1488, 1442, 1360, 1327, 1255, 1221, 1155, 1064, 1023, 883, 851, 774, 756, 705, 629, 570, 539, 514, 447 cm^{-1}. HRMS (ESI): *m/z* calcd. for $C_{22}H_{18}N_2$ [M]$^{2+}$ 155.0730, found 155.0740.

1-Methyl-2-(phenylethynyl)quinolinium methylsulfate (4g): According to Procedure 3, a solution of 0.057 g (0.25 mmol) of 2-(phenylethynyl)quinoline **3g**, 1 drop of nitrobenzene and 0.06 mL (0.63 mmol) of dimethyl sulfate in 6 mL of anhydrous toluene was heated for 3 h under reflux temperature to give 1-methyl-2-(phenylethynyl)quinolinium methylsulfate **4g**. Yield 0.085 g, 96 %, a yellow solid, m.p. 119–120 °C (decomp.). ^{1}H NMR (600 MHz, DMSO[D$_6$]): δ = 9.23 (d, J = 8.6 Hz, 1H, 4-H), 8.59 (d, J = 8.9 Hz, 1H, 8-H), 8.46 (d, J = 7.8 Hz, 1H, 5-H), 8.43 (d, J = 8.6 Hz, 1H, 3-H), 8.32–8.29 (m, 1H, 7-H), 8.05 (t, J = 7.5 Hz, 1H, 6-H), 7.97–7.95 (m, 2H, 2′-H, 6′-H), 7.71–7.68 (m, 1H, 4′-H), 7.64–7.61 (m, 2H, 3′-H, 5′-H), 4.78 (s, 3H, NCH$_3$), 3.37 (s, 3H, CH$_3$SO$_4$) ppm. ^{13}C NMR (150 MHz, [D$_6$]DMSO): δ = 145.4 (+, C4), 140.8 (o, C2), 139.3 (o, C8a), 136.0 (+, C7), 133.1 (+, C2′, C6′), 132.4 (+, C4′), 130.3 (+, C5), 130.0 (+, C6), 129.3 (+, C3′, C5′), 128.4 (o, C4a), 126.2 (+, C3), 119.5 (+, C8), 118.8 (o, C1′), 108.6 (o, Cβ), 82.7 (o, Cα), 52.8 (+, CH$_3$SO$_4$), 42.8 (+, NCH$_3$) ppm. IR (ATR): 3531, 3474, 3062, 3016, 2980, 2941, 2199, 1618, 1601, 1576, 1520, 1441, 1359, 1311, 1243, 1221, 1155, 1060, 1003, 875, 844, 774, 745, 687, 611, 577, 542, 501, 426 cm^{-1}. HRMS (ESI): *m/z* calcd. for $C_{18}H_{14}N$ [M]$^+$ 244.1126, found 244.1131.

1-Methyl-4-(phenylethynyl)quinolinium methylsulfate (4i): According to Procedure 3, a solution 0.057 g (0.25 mmol) of 4-(phenylethynyl)quinoline **3i**, 1 drop of nitrobenzene and 0.06 mL (0.625 mmol) of dimethyl sulfate in 6 mL of anhydrous toluene was heated over the period of 1.5 h under reflux temperature to give 1-methyl-4-(phenylethynyl)quinolinium methylsulfate **4i**. Yield 0.088 g, 100 %, a yellow solid, m.p. 165–166 °C. ^{1}H NMR (600 MHz, [D$_6$]DMSO): δ = 9.49 (d, J = 6.4 Hz, 1H, 2-H), 8.77 (d, J = 8.2 Hz, 1H, 5-H), 8.55 (d, J = 8.8 Hz, 1H, 8-H), 8.36 (d, J = 6.0 Hz, 1H, 3-H), 8.34 (ddd, J = 1.3, 7.1, 8.7 Hz, 1H, 7-H), 8.17–8.14 (m, 1H, 6-H), 7.92-7.91 (m, 2H, 2′-H, 6′-H), 7.66–7.64 (m, 1H, 4′-H), 7.61-7.58 (m, 2H, 3′-H, 5′-H), 4.63 (s, 3H, NCH$_3$), 3.37 (s, 3H, CH$_3$SO$_4$) ppm. ^{13}C NMR (150 MHz,

[D_6]DMSO): δ = 149.4 (+, C2), 138.5 (o, C4), 138.4 (o, C8a), 135.7 (+, C7), 132.8 (+, C2′, C6′), 131.5 (+, C4′), 130.8 (+, C6), 129.2 (+, C3′, C5′), 128.4 (o, C4a), 127.9 (+, C5), 124.2 (+, C3), 119.9 (o, C1′), 119.8 (+, C8), 107.3 (o, Cβ), 84.1 (o, Cα), 52.8 (+, CH_3SO_4), 45.3 (+, NCH_3) ppm. IR (ATR): 3022, 2944, 2199, 1605, 1575, 1529, 1496, 1441, 1400, 1374, 1325, 1224, 1059, 1012, 840, 766, 731, 691, 608, 575, 546, 533, 503, 469, 430 cm^{-1}. HRMS (ESI): *m/z* calcd. for $C_{18}H_{14}N$ $[M]^+$ 244.1126, found 244.1117.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

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