Optimization of the Substitution Pattern of 1,3-Disubstituted Imidazo[1,5-a]Pyridines and -Quinolines for Electro-Optical Applications

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A series of recently synthesized 1,3-disubstituted imidazo[1,5-a]pyridines (IPs) and -quinolines (IQs) targeting at increased efficiency of luminescence is investigated. The properties of molecules in solution as well as their change in the solid state are reported and assessed regarding possible application in organic electronics. The influence of increased ring size by substitution, e.g., exchanging phenyl to naphthalenyl, as well as pyridyl to quinolinyl moieties, and by means of a larger IQ fluorophore is discussed. A higher oscillator strength and quantum yield can be achieved. Frontier orbital energies are estimated based on cyclic voltammetry and density functional theory (DFT) calculations. Single crystals of molecules are grown. A red-shift in the photoluminescence spectra found for crystals of IQs compared with those in solution is proposed to be caused by intermolecular coupling based on the parallel stacking of the enlarged fluorophore units. Thin films deposited by physical vapor deposition exhibit similar effects, showing promise as active layers in organic light-emitting diodes (OLEDs). An amorphous morphology is inferred for these films from both spectral broadening in photoluminescence and atomic force microscopy. An OLED test structure is prepared, using the most efficient IQ lumophore and demonstrating the feasibility of obtaining electroluminescence from such thin films.

1. Introduction

Organic fluorophores are well-established functional molecules, used as luminescent probes in medicine and biology,[1,2] as photonic materials,[3] or in organic electronics.[4] Since the first work on organic light-emitting diodes (OLEDs) by Tang and VanSlyke,[5] such devices have attracted significant attention and are now part of state-of-the-art displays.[6–11] In this context, key performance parameters as well as new unique characteristics can be influenced or introduced by novel fluorophores.

Blue light-emitting 1,3-disubstituted imidazo[1,5-a]pyridines (IPs) and their imidazo[1,5-a]quinoline (IQ) homologues have shown quantum yields up to 44%, possess large Stokes shifts, and can be prepared by facile synthetic methods.[12–17] IQs have exhibited suitable material properties for application in OLEDs.[14,15] Using 1-(pyridin-2-yl)-3-(quinolin-2-yl)imidazo[1,5-a]quinoline in a layer architecture with typical contact materials, blue OLEDs were prepared recently.[18] The substitution with different functional groups up to now has mainly been studied on the IP core.[12–14,17,19–22] The increase in the size of the π-system at the chromophore unit can affect quantum yield[21] and absorbance wavelength, determined by the gap between frontier orbitals.[24,25] In addition, such a change in orbital energy might be influenced by the twisting of the π-system,[26] as a consequence of introduced functional moieties perturbing conformation. In the context of improving optical properties, the further exploration of such effects on IP derivatives and an extension of such a study on the group of IQs are, therefore, useful in an assessment for application in OLEDs.

Consequently, in addition to molecular properties, studies on fluorophores in the solid state are required. Single crystals consist of highly ordered organic molecules, providing insight

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to molecular interaction at close proximity. The π-systems of molecules may interact, leading to π-π stacking.[27] Therefore, charge carrier mobility is affected by the crystalline structure[27,28] and in particular, the coupling of electronic wave functions, which is depending on molecular arrangement that influences luminescence energy and intensity compared with isolated or dissolved molecules.[29–31] In contrast to crystals, but depending on the preparation conditions, thin films (TFs) of organic molecules are often amorphous rather than crystalline. Charge carrier mobility in such amorphous layers, which is based on hopping transport, is also dependent on the extent of electronic coupling.[32] Furthermore, to effectively inject charge carriers into TFs, knowledge on the energy of the frontier orbitals is needed. The work function of adjacent layers has to be close in energy to the respective orbital to minimize the barrier for the injection of charge carriers. Physical vapor deposition (PVD) serves as a suitable method to prepare such TFs and interfaces because it often leads to pure and homogeneous layers.[33,34] Despite advantages of alternative solvent-based film preparation, PVD is, therefore, often also used in technical device preparation.[34]

In this work, the step-wise change of physical properties was investigated for a range of five differently substituted IPs and IQs each. Absorption and emission spectra as well as quantum yields were measured in solution and interpreted based on density functional theory (DFT) calculations. The effects on the energy of the highest-occupied molecular orbital (HOMO) were studied by cyclic voltammetry and analyzed. For a representative choice of molecules, single crystals were grown and TFs were prepared by PVD. Time-resolved and steady-state photoluminescence of the molecules was used to assess the degree of intermolecular coupling. Furthermore, thin-film morphology was derived from the spectroscopic measurements and verified by atomic force microscopy (AFM). To demonstrate applicability to OLED technology, a simple test device with the most efficient lumophore in the active layer was built.

2. Results and Discussion

The investigated molecules IP1–IP5 and IQ1–IQ5 are shown in Table 1 with their structure formula in Figure 1. Different moieties were chosen at R and R’ to study their effects on molecular properties. In particular, the distribution of the conjugated π-orbitals is of interest. This property changes when comparing IP1 with IP4, for example, going from a phenyl to a naphthalenyl moiety at R, or from IP4 to IQ1, exchanging the IP to an IQ core. The phenyl and naphthalenyl moieties furthermore are replaced by pyridyl and quinolinyl groups, e.g., when comparing IP1 with IP3 or IQ1 with IQ2, which can, for example, influence orbital energies.[35] Fluorination (IQ4 and IQ5) as well as methoxylation (IP2) have shown to improve optical properties in a previous work.[21] As some characteristics of solutions and crystals of IQ3 have already been reported earlier,[15] these data are used in Table 2 and 3 as well as in Figure 2, 3, 4, 5, and 6.

### Table 1. Molecules investigated in this study. R and R’ are shown in Figure 1.

| IP1 | Phenyl | Phenyl |
| IP2 | Phenyl | 4-Methoxyphenyl |
| IP3 | Pyridin-2-yl | Pyridin-2-yl |
| IP4 | Naphthalenyl | Phenyl |
| IP5 | Naphthalenyl | Pyridin-2-yl |
| IQ1 | Naphthalenyl | Phenyl |
| IQ2 | Phenyl | Pyridin-2-yl |
| IQ3 | Quinolin-2-yl | Pyridin-2-yl |
| IQ4 | Naphthalenyl | 4-Fluorophenyl |
| IQ5 | Quinolin-2-yl | 4-Fluorophenyl |

### Table 2. Extracted optical properties as measured in 0.1 mM chloroform solution.

| λ_{ex} [nm] | Extinction | Luminescence |
|-----------|------------|-------------|
| IP1 | 454 | 2.73 | 0.09 | 401 | 481 | 9 |
| IP2 | 438 | 2.83 | 0.09 | 407 | 473 | 8 |
| IP3 | 459 | 2.70 | 0.16 | 401 | 444 | 9 |
| IP4 | 433 | 2.86 | 419 | 488 | 420 | 496 |
| IP5 | 430 | 2.88 | 0.23 | 414 | 476 | 35 |
| IQ1 | 423 | 2.93 | 0.23 | 414 | 476 | 28 |
| IQ2 | 421 | 2.95 | 0.19 | 411 | 463 | 14 |
| IQ3 | 420 | 2.88 | 0.27 | 412 | 460 | 28 |
| IQ4 | 432 | 2.87 | 0.23 | 414 | 476 | 28 |
| IQ5 | 432 | 2.87 | 0.23 | 414 | 467 | 35 |

### Table 3. Photoluminescence properties of crystals and TFs.

| TF absorption | TF luminescence | Crystal luminescence |
|---------------|-----------------|---------------------|
| TF absorption | TF luminescence | Crystal luminescence |
| Edge [nm] | Opt. gap [eV] | Edge [nm] | Peak [nm] | Edge [nm] | Peak [nm] |
| IP1 | 443 | 2.80 | 413 | 489 | 427 | 489 |
| IP2 | 434 | 2.86 | 419 | 488 | 420 | 496 |
| IP3 | 446 | 2.78 | 427 | 484 | 429 | 484 |
| IP4 | 436 | 2.84 | 420 | 498 | 430 | 512 |
| IP5 | 448 | 2.77 | 421 | 485 | 445 | 491 |

![Figure 1. Structure formula of the investigated 1,3-disubstituted IP (black) and IQ (added gray area). R and R’ are shown in Figure 1.](image-url)
To investigate optical properties, light extinction and photoluminescence measurements were carried out. Chloroform as a solvent has been shown to be suitable for such experiments, as it dissolves most of the target molecules, but it does not significantly influence electronic and optical properties.

### 2.1. Structure and Energy Levels of Isolated Molecules

Figure 2 shows exemplary extinction spectra (see Figure S2, Supporting Information, for other spectra), and the extracted properties of all molecules investigated are shown in Table 2. The optical gap energy was obtained by a linear fit of the extinction edge $\lambda_{e}$ and converting the intersection wavelength into an energy value. The oscillator strength of the absorption process, depending on the transition dipole moment and overlap of the initial- and final-state wave functions, was determined by integration of the spectra from 2 to $3 \times 10^{4}$ cm$^{-1}$ (500–333 nm) and calculated according to $f = 4.32 \times 10^{-9} / n \times \int \varepsilon(\nu) d\nu$. As a starting point, IP1 shows a broad, flat extinction with no clear maximum. An oscillator strength of $f = 0.09$ is derived and the transition is, thereby, assigned to a $\pi-\pi^*$ transition.

The introduction of a methoxy group for IP2 has no significant effect on absorption. Increasing the aromatic system R to a naphthalenyl moiety, e.g., for IP4 leads to a small increase to $f = 0.10$. Upon introduction of a pyridyl moiety, $f$ significantly increases, as is the case when comparing IP1 with IP3 or IP4 with IP5. The molecular conformation in the ground state calculated by DFT and the corresponding frontier orbital wave functions are shown in Figure 7 for a representative group of molecules (see Figure S3 and S4, Supporting Information, for data of other compounds). The introduction of a nitrogen atom at position 2 into R or R$^0$ (IP3, IP5, IQ2, IQ3, and IQ5) leads to a planarization of this peripheral moiety with the core of the molecule, which is presumably due to the missing repulsion of the hydrogen atom previously bound to the replaced carbon. In addition, a small interaction between the lone pair of nitrogen and the neighboring hydrogen atom at the core might support the

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**Figure 2.** Extinction spectra of exemplary molecules as measured in 0.1 mM chloroform solution.

**Figure 3.** Normalized and offset photoluminescence spectra of exemplary molecules in 0.1 mM chloroform solution.

**Figure 4.** Cyclic voltammograms of exemplary molecules (5 mM) in 0.1 M TBABF$_4$/DMF solution at a scan rate of 50 mV s$^{-1}$. 
Planarization. An example is shown for IP1 and IP3 in Figure 7. Planarization directly influences the magnitude of the transition dipole by increasing orbital distribution and/or overlap of the wave functions for ground and excited states. In the case of IP1, the HOMO is spread over the whole molecule, whereas the calculated empty lowest-unoccupied molecular orbital (LUMO) as an approximation for the excited state is located on one of the twisted side groups, R or R’ only. For IP3, the π-orbitals on R’ are in plane and the LUMO is extended to both peripheral pyridyl groups. The optical gaps for all IPs are roughly identical at 2.80 ± 0.08 eV.

When exchanging the IP to an IQ, as can be seen from IP4 to IQ1, f increases significantly, which can be further improved by the introduction of nitrogen atoms at position 2 in R and R’ (see IQ1–IQ3). DFT calculations show that R’ is twisted out of the imidazo plane for all IQs studied, as there is a hindrance by the hydrogen atom at position 6 on the core (Figure 1) for the R’ side group to be planar (IQ5 in Figure 7). Both HOMO and LUMO are mainly centered on an axis from R along the core of the molecule. The hydrogen atom at position 2 of R0 with 4-fluoro-phenyl moiety leads to a further twist of R’, whereas with a pyridyl group at R’ (IQ3 and IQ2), frontier orbitals include the side group. In case of IQ2, the LUMO even shifts from Rt to R0. The optical gap at 2.91 ± 0.03 eV does not significantly change among the IQs investigated and is slightly larger than that for the smaller pyridine IP homologue.
Exemplary photoluminescence spectra (see Figure S2, Supporting Information, for spectra of other compounds) are shown in Figure 3. The emission edges determined by a linear fit and the peak position are shown in Table 2 together with the quantum yield Φ. The emission spectra resemble each other, with their edge at 410 ± 6 nm, following the trend given by the respective absorption edge. Molecules with a nitrogen-containing moiety at R are observed to have a spectrum shifted toward higher energies. Presumably, a more rigid molecular conformation leads to such a higher energy of the excited state. The emission quantum yield Φ closely follows the trend given by the peak position in the material. To estimate the HOMO, the oxidation onset can be obtained by the average of peak potentials $E_{\text{ox}}^\text{ox} = (E_{\text{ox}}^+ + E_{\text{red}}^-)/2$, which are also shown in Table 4. As this method, however, cannot be applied for IQs, the discussion is based on the values of $E_{\text{ox}}^\text{ox}$. The oxidation onset of IPs is found at 480 ± 57 mV versus Fc/Fc$^+$ (Table 4). Details of the substitution pattern do not lead to significant differences with the exception of the methoxy moiety in IP2, which has a significant electron-donating effect, leading to a less-positive $E_{\text{ox}}^\text{ox}$, and an increase in HOMO energy. For IP2, a second oxidation wave is observed, which can be assigned to a second, reversible oxidation.

In contrast, the IQs in this study do not show chemical reversibility in their oxidation waves. Previous measurements on IQ3 with different scan rates[39] could be explained by a chemical reaction, which removed the oxidized molecules from the electrodes and thereby hindered their rereduction.[40] The oxidation onsets of IQs are found at a higher potential of 660 ± 60 mV versus Fc/Fc$^+$, and the HOMO is found at lower energies for IQs than for the IP homologues. DFT calculations yield a HOMO concentrated along the IQ core and R, showing that by twisting R' out of the imidazo plane a different electronic system is affected by oxidation of IQ compared with IP with their larger contribution of R'. A second oxidation is found for IQ1 and IQ4, indicating that the naphthalenyl moiety is the reason when comparing with IQ2 or IQ5, respectively.

The trend of calculated HOMO energies fits well with the values determined by electrochemistry with a mean difference of 135 ± 80 meV between calculation and electrochemical methods. The absorption onset of IQ compared with IP with their larger contribution of R'. A second oxidation is found for IQ1 and IQ4, indicating that the naphthalenyl moiety is the reason when comparing with IQ2 or IQ5, respectively.

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### Table 4. Electrochemically determined HOMO energy and calculated theoretical frontier orbital energy.

| Compound | $E_{\text{ox}}^\text{ox}$ | $E_{\text{ox}}^\text{red}$ | $E_{\text{HOMO}}$ | $E_{\text{LUMO}}$ | $E_{\text{CAP}}$ |
|----------|----------------|----------------|----------------|----------------|----------------|
| IP1      | 0.50           | 0.37           | 5.30           | 5.24           | 1.47           | 3.77           |
| IP2      | 0.39           | 0.34           | 5.15           | 5.09           | 1.40           | 3.69           |
| IP3      | 0.56           | 0.46           | 5.38           | 5.27           | 1.53           | 3.74           |
| IP4      | 0.50           | 0.39           | 5.30           | 5.18           | 1.54           | 3.64           |
| IP5      | 0.45           | 0.37           | 5.23           | 5.21           | 1.55           | 3.66           |
| IQ1      | 0.60           | –              | 5.44           | 5.28           | 1.73           | 3.35           |
| IQ2      | 0.73           | –              | 5.62           | 5.35           | 1.79           | 3.56           |
| IQ3      | 0.70           | –              | 5.58           | 5.39           | 1.92           | 3.47           |
| IQ4      | 0.59           | –              | 5.43           | 5.38           | 1.85           | 3.53           |
| IQ5      | 0.69           | –              | 5.57           | 5.45           | 1.97           | 3.48           |

*aVersus Fc/Fc$^+$.**
experiment. As DFT calculations were carried out for isolated molecules without any dielectric environment and electrochemistry does include the effects of solvent and intermolecular interaction, such deviation is expected. The energy difference $E_{\text{GAP}}$ between HOMO and LUMO (Table 4) is $3.7 \pm 0.05$ eV for IPs and reduced to $3.5 \pm 0.04$ eV for IQs. Such a clear trend is remarkable in view of the variety of substituents. The decrease in $E_{\text{GAP}}$ indicates an increased delocalization of electrons in the $\pi$-system of the studied IQs, which is expected in view of the increased ring size.

The experimental optical absorption gap of both homologues (Table 2) is found at $2.80 \pm 0.08$ eV for IPs and is slightly larger for IQs with $2.91 \pm 0.03$ eV. A comparison with the values of $E_{\text{GAP}}$ suggests a stronger stabilization of the electronically excited state in IPs compared with IQs.

2.2. Structure and Electronic Coupling in Crystals and Thin Solid Films

For a discussion of application in organic electronics, solid-state properties are of prominent interest. Therefore, crystals were grown to study such highly ordered assemblies of molecules. Entrainer sublimation produced crystals of IP5, IQ3, IQ4, and IQ5. The crystals of IP1 and IP2 were obtained by solvent diffusion. Crystal structures could be determined by X-ray diffraction (XRD) for IP1, IP2, IQ3, IQ4, IQ5, and IQ5 and unit cells are shown in Figure 8. The density of molecules in the crystal lattice is $1.332 \text{ g cm}^{-3}$ for IP1, $1.333 \text{ g cm}^{-3}$ for IP2, whereas IQ3, IQ4, and IQ5 exhibit a density of $1.390, 1.412$, and $1.421 \text{ g cm}^{-3}$, respectively. The molecular conformation found in unit cells shows that the structure optimized for isolated molecules (Figure 7) is widely preserved in the solid state (Figure 8), speaking in favor of rather small intermolecular lattice energies compared with intramolecular binding energies. The twisting of $\mathbf{R}_0$ in case of the IQs as well as planarization of $\mathbf{R}$ or $\mathbf{R}_0$ for pyridyl and quinolinyl moieties is observed, demonstrating the stability of individual molecular conformation in the presence of intermolecular interactions. For IP1 and IP2, both $\mathbf{R}$ and $\mathbf{R}_0$ are twisted out of plane, whereas, for example, $\mathbf{R}$ on IQ5 is almost in plane with the quinoline core. A similar behavior is seen for $\mathbf{R}$ and $\mathbf{R}_0$ on IQ3 in comparison with IQ4.

In the crystal lattice of IP1, the molecules are all facing in the same direction, so IP cores are aligned in a row. In the orthogonal direction of the cores, e.g., in the direction of $\pi$-orbitals, IP1 molecules are not stacking cofacial, as one molecule is shifted by half a core length from direct overlap, leading to parallel displacement. For IP2, IP cores of adjacent molecules are roughly oriented toward each other but are not parallel regarding their $\pi$-systems. These planes are separated by $\mathbf{R}_1$, whose phenyl moieties are also not parallel to each other. A parallel displaced structure is observed. The crystal structure of IQ3 was previously found to have IQ cores and $\mathbf{R}$ of adjacent molecules stacked cofacial but in two planes almost orthogonal to each other. An almost parallel, cofacial arrangement of IQ cores and $\mathbf{R}$ is also observed for all molecules in the IQ4 and IQ5 structure, however, with a rotated $\mathbf{R}_0$ in between. Separation of the two molecules in the unit cell is dependent on the degree of twist for $\mathbf{R}$; they are closer for IQ5 than for IQ4. Planarization in the imidazo plane, therefore, has a significant influence on crystal structure. As the imidazo plane represents the plane of the frontier orbitals (Figure 7), such a molecular arrangement in the unit cells of IQs leads to a preferentially parallel arrangement of HOMO and LUMO. Such an interaction of $\pi$-orbitals can serve to stabilize the structure.

The photoluminescence of crystals was investigated by fluorescence microscopy. Figure 5 shows the results in comparison with emission in chloroform solution and thin-film samples on quartz, whereas Table 3 shows the results. Earlier work has shown a strong red-shift of photoluminescence for crystals of IQ3 from spectra measured in solution, indicating a clear influence of molecular coupling in the crystal. A similar behavior is found for IQ4 and IQ5, which is plausible in view of the similar, intermolecular arrangement, in particular, of the $\pi$-orbitals, which determines the strength of coupling. In consequence, IQ5 displays a stronger red-shift than IQ4, corresponding well to the smaller distance between molecules of IQ5 in the unit cell.

IP1, IP2, and IP5 do not display red-shifted emission. In case of IP1 and IP2, this can be explained by a nonparallel molecular arrangement, which might also be the case for IP5 (no structure obtained). It is seen that a comparison of crystal photoluminescence compared with that in solution can be utilized to show the degree of intermolecular coupling in the crystal structure. Such coupling is important for organic electronics to discuss charge transport. TFs of molecules IP2, IP5, IQ3, IQ4, and IQ5, as typical for application in organic electronics, were prepared under identical experimental parameters by PVD. The photoluminescence of these TFs is shown in Figure 5.

For IP2 and IP5 TFs, the spectral shape of the photoluminescence is similar to that of crystals (and solution); missing, however, are the pronounced features of vibrational modes or optical interference in the crystals. In case of IQ3, the thin-film emission spectrum is also red-shifted, compared with that in solution, as seen in a previous work. For IQ4 and IQ5, the spectrum of the TF is centered at a comparable wavelength to that found for the crystal, with its edge close to the spectrum of the solution, indicating weaker coupling in the TF. In all cases, the emission of TFs is broader and does present less-distinct
A comparison of the molar volume of IQs in the crystal lattices does not display significantly closer packing for IQ3 (267.9 cm$^3$ mol$^{-1}$) for IQ3, 275.1 cm$^3$ mol$^{-1}$ for IQ4, and 274.1 cm$^3$ mol$^{-1}$ for IQ5). Assuming, therefore, a similar trend of density in the amorphous TFs, and a similar influence of the dielectric environment, the increased absorption of IQ3 is presumably caused by a specific coupling of chromophores in the solid.

The determination of the excited state lifetime in solid samples gives direct access to the influence of solid-state effects on photoluminescence when compared with that of dissolved molecules. Fluorescence decay in solution was fitted with a monoexponential decay function, whereas TFs had to be fitted by a biexponential decay to obtain satisfactory precision. Results are shown in Figure S5, Supporting Information, and in Table 5.

The average lifetime in the TFs of IP2, IP5, IQ4, and IQ5 is slightly decreased when compared with measurements in solution. Presumably, this is due to an increase in nonradiative decay caused by intermolecular interaction. For IQ3, the excited state lifetime is significantly lower in the solid. This might be caused by an even higher nonradiative decay rate than for other IQs. Alternatively, the short lifetime of the excited state of IQ3 could stem from a higher radiative rate. In solution, IQ3 has the highest f among IQs and absorption of IQ3 TFs was even found to be increased in relation to the other IQs studied (Figure 9), suggesting a positive influence of solid-state interaction on the radiative rate.

As a first step to show the applicability of the studied class of molecules in electro-optical devices, a prototype OLED structure was prepared with IQ5, which shows the highest molecular photoluminescence quantum yield (Table 2). Suitable contact materials, able to inject charge carriers, fitting to the frontier orbital energies and a layer architecture already developed for IQ3 have been used, and a model device ITO/PEDOT:PSS/IQ5/BCP/Al has been prepared by spin coating (PEDOT:PSS) and PVD (all other layers) on a commercial indium tin oxide (ITO) substrate. The results of this test OLED with IQ5 as an active emitting layer are shown in Figure 10. The spectrum obtained does fit well to the photoluminescence signal found for the corresponding TF regarding peak position and shape, no signals specific for crystalline domains or isolated molecules are seen beyond this. It is thereby shown that the amorphous arrangement of molecules, which is dominant in TFs, can also be electrically addressed and work as an emitter layer. This was also seen before for IQ3 in the same contacting scheme. The diode produces blue/greenish-white electroluminescence at stable electrical performance and reasonable current density (the inset in Figure 10). Its emission color according to the CIE 1931 XYZ color space with a 2° observer is found at $x = 0.27$, $y = 0.36$, and $z = 0.37$. The visual impression looks similar to the observed photomission (see photographs in Table of Contents figure). The rather high value of the threshold voltage, as also previously seen for IQ3, indicates high barriers for charge carrier injection in the present test structure. Therefore, optimization of the device architecture is clearly needed and may further improve such OLEDs with IQ emitters. Nevertheless, at driving voltages}

| Solution | $\tau_1$ [ns] | $\tau_2$ [ns] | $a$ | $X^2$ | $\tau_{avg}$ [ns] |
|----------|--------------|--------------|-----|-------|------------------|
| IP1      | 1.9          | 35.5         | 1.7 | 6.3   | 0.84             |
| IP2      | 2.3          | 18.5         | 5.3 | 0.70  | 1.4              |
| IP5      | 2.1          | 9.4          | 1.7 | 6.3   | 0.84             |
| IQ3      | 1.9          | 6.5          | 0.5 | 5.3   | 0.98             |
| IQ4      | 2.3          | 8.8          | 1.8 | 6.4   | 0.91             |
| IQ5      | 2.3          | 14.5         | 1.3 | 6.3   | 0.72             |

Table 5. Measured excited-state lifetime of molecules at 20 μM in chloroform and of TFs.
above the threshold voltage of about 16.5 V, it can be assumed that all contacts become conducting and that the emissive layer limits the current. A lower limit of the electrical conductivity of 1.2 x 10⁻² S cm⁻¹ for IQ5 was, therefore, determined from a fit to the linear part, which is quite common for organic semiconductors.¹³⁴

3. Conclusion

Starting at 1,3-diphenyl imidazo[1,5-a]pyridine as the most simple molecule of this study, the influence of the enlarging ring size at substitutional groups R and R', as well as when using larger IQs, was examined. Oscillator strength and quantum yield are increased and are significantly higher on IQs investigated. Quantum yields, therefore, can be improved using such a higher homologue core. In addition, pyridyl and quinolinyl moieties were introduced at R and R', rotating side groups in plane to the fluorophore core and thereby extending frontier orbitals, as seen by DFT. This also leads to increased absorption. IQs have, thereby, been identified as a promising motif in luminescent molecules, building on the established IQs.

Cyclic voltammetry was used to investigate oxidation properties, reporting oxidation onsets and HOMO energies. IQs are more stable against oxidation yet prone to irreversible consecutive chemical reaction once oxidized. In contrast, IPs are stable in the oxidized state. Functional moieties on R and R' were concluded to have minor effects when compared against an increase in electron binding from –5.27 ± 0.08 eV for IPs to –5.53 ± 0.08 eV for IQs. The quantum chemical calculations reproduce the trend, showing a change in HOMO and LUMO locations from being spread over most of the IP molecule to an axis of core to R on the larger IQ homologues. Furthermore, frontier orbitals of the investigated IQs are located mainly on an axis of the fluorophore core and R due to a rotation of R'.

Such conformation is supported by single-crystal XRD. In the crystals, the molecules are stacked with this axis in parallel. In consequence, the crystals of IQs exhibit a large red-shift of photoluminescence compared with isolated molecules in solution. This can be assigned to intermolecular coupling and is not observed for the investigated IPs. TFs also exhibit intermolecular coupling, but to a lesser extent, which is reaffirmed by a shift of absorption spectra relative to those in solution. The decrease is attributed to an amorphous film structure in most cases, deduced from a broadening of photoluminescence spectra. In confirmation, AFM reveals smooth, amorphous TFs of IP2, IQ4, and IQ5, similar in film morphology to IQ3. IQ3 is found to be the strongest absorber for thin-film samples because of the specific intermolecular coupling of chromophores. IQ5, however, does possess a higher molecular fluorescence quantum yield. An OLED test structure containing IQ5 as the emitter layer was built, demonstrating its feasibility in such device architectures. In conclusion, IQs have been proven as attractive structural motifs, allowing further molecular optimization and advanced device engineering.

4. Experimental Section

The molecules IP1, 1,3-diphenylimidazo[1,5-a]pyridine, IP2, 3-(4-methoxyphenyl)-1-(phenyl)imidazo[1,5-a]pyridine, IP3, 1,3-di(pyrindin-2-yl)imidazo[1,5-a]pyridine, IP4, 1-(naphthalen-1-yl)-3-(phenyl)imidazo[1,5-a]pyridine, IQ5, 1-(naphthalen-1-yl)-3-(pyridin-2-yl)imidazo[1,5-a]pyridine, IQ1, 1-(naphthalen-1-yl)-3-(pyridin-2-yl)imidazo[1,5-a]quinoline, IQ2, 3-(pyridin-2-yl)-1-(phenyl)imidazo[1,5-a]quinoline, IQ3, 1-(pyridin-2-yl)-3-(quinolin-2-yl)imidazo[1,5-a]quinoline, IQ4, 3-(4-fluorophenyl)-1-(2-naphthalenyl)imidazo[1,5-a]quinoline, and IQ5, 3-(4-fluorophenyl)-1-(2-quinolinyl)imidazo[1,5-a]quinoline were synthesized as described by Albrecht et al.¹³⁵ and purified by sublimation in high vacuum. Extinction measurements in the ultraviolet and visible spectral region (UV–vis) of solutions were carried out with a JASCO V-760 spectrometer at 10 μM concentration in chloroform. The corresponding emission properties were investigated with a Jasco Germany FP-8300 spectrometer. The fluorescence quantum yield (Φ) of the materials was measured in chloroform (n = 1.445)¹⁵⁶ calibrated against an equally concentrated quinine sulfate solution (Φ = 0.546 and refractive index n = 1.339)¹⁶⁹. Fluorescence lifetime measurements were carried out on 20 μM solutions of the molecules in chloroform. A scattering solution of ZnO nanoparticles (40 nm diameter) was used to obtain the instrument response function (IRF). In case of thin-film measurements, a roughened Ted Pella Inc. GE124 quartz glass slide served as the scattering probe instead. An IBN FluoroCube was used with a 370 nm IBN LED as the excitation source and a 380 nm bandpass filter. DecayFit 1.3 was used for data analysis and fitting.¹⁶⁶ Solution data were fitted with a single-exponent decay function y = a * exp(–t/τ) and thin-film data were fitted with a second term according to y = a * exp(–t/τ1) + (1 – a) * exp(–t/τ2). For cyclic voltammetry, a 5 μm dimethylformamide (DMF) solution (Carl Roth GmbH) of the analyte using 0.1 M tetrabutylammonium tetrafluoroborate (TBABF₄, Sigma Aldrich) as a supporting electrolyte was prepared. Platinum wires were used as the working and counter electrodes and a leak-free Ag/AgCl electrode (LF-2, Warner Instruments) as the reference electrode. Ferrocene (Fc) (Sigma Aldrich >98%) was used as internal reference. All electrochemical measurements were carried out in a water and oxygen-free environment (<0.3 ppm) with an Ivium Technologies IviumStat potentiostat at 50 mV s⁻¹ scan rate. The molecular full-feature optimizations by DFT, without symmetry restrictions, were conducted using the Gaussian 16 Revision B.01 software package with the hybrid exchange correlation functional B3LYP¹⁴⁷–⁴⁹ and a def2-TZVP¹⁰⁵,¹¹¹ basis set. Crystals were prepared either by solvent evaporation or by entrainer sublimation in a KOYO Thermo Systems Co. Ltd. KTF030N oven. TFs were prepared in a jeol JEE-400 vacuum evaporator by PVD or in a self-made evaporation chamber under high vacuum. The material was evaporated
from a resistively heated crucible at evaporation rates of about 1 nm min\(^{-1}\), measured in situ by a quartz crystal microbalance (QCM). TFs of IP\(^1\) could not be deposited by this method. AIST-NR SmartSPM with Seiko Instruments SEIHR tips was used for all AFM measurements, analyzed by GWYDDION 2.47. The average film thickness was determined mainly by AFM. In case of IP\(^2\), the grains of materials, seen in the scan shown in Figure 6, were marked and their volume converted to that of a uniform film, with a rectangular cross-section of the same volume. Film thickness of IQ\(^3\) was determined by QCM using a film density of 1.5 g cm\(^{-3}\).[17] As an approximation for the crystalline film of IP\(^3\), the minimum of all available data points was set to zero, assuming to be the quartz glass surface. The maximum of height distribution was then interpreted as average film thickness. In case of IQ\(^4\) and IQ\(^5\), the films were scratched by a plastic spatula, exposing the quartz surface. The film thickness was then measured by averaging the height obtained from line scans of the edge. Thin-film absorbance was investigated with an Analytics Jena Spectro 40 UV/vis spectrometer. The emission of TFs and crystals was measured in a fluorescence microscope with a Hamamatsu Photonics PMA-12 CCD spectrometer at 365 nm excitation from a mercury lamp through an optical filter. OLED preparation was adopted from a previous work.[27] Bathocuproine (BCP, (>99.99%) and poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) were obtained from Ossila, ITO-coated glass from Zhuhai Kaivo Optoelectronic Technology Co., Ltd. Devices were structured with a layer order of ITO/PEDOT:PSS/ PMA-12 CCD spectrometer at 365 nm excitation from a mercury lamp through an optical filter. The authors declare no conflict of interest.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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**Conflict of Interest**

The authors declare no conflict of interest.

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