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2,11-Dialkylated 1,12-Diazaperylene Copper(I) Complexes: First Supramolecular Column Assemblies by π-π Stacking between Homoleptic Tetrahedral Metal Complexes, Exhibiting Low-Energy MLCT Transitions

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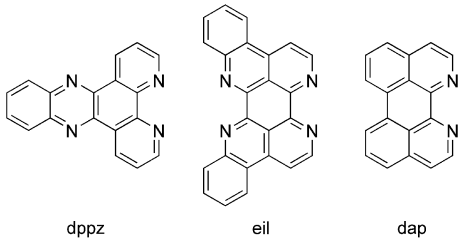
2,11-Dialkylated 1,12-diazaperylenes (alkyl = Me, Et, *i*Pr) dmedap, detdap and dipdap have been synthesized by reductive cyclization of 3,3′-dialkylated 1,1′-biisoquinolines **3a–c**, resulting in the first copper(I) complexes of a "large-surface" ligand. The new copper(I) complexes show low-energy MLCT absorptions unprecedented for bis(α-diimin)-copper(I) complexes. The solid structures of the complexes $[Cu(dipdap)_2]BF_4 \cdot CH_2Cl_2 \cdot 1.5H_2O$, $[Cu(dipdap)_2]OTf \cdot CH_2Cl_2$, $[Cu(dipdap)_2]I \cdot C_2H_4Cl_2 \cdot THF \cdot 2H_2O$, $[Cu(dmedap)_2]OTf$ and $[Cu(dipdap)_2]AQSO_3 \cdot H_2O$ ($AQSO_3$ = sodium 9,10-dihydro-9,10-dioxo-2-anthracenesulfonate) are reported. In $[Cu(dipdap)_2]BF_4 \cdot CH_2Cl_2 \cdot 1.5H_2O$, each copper(I) complex cation interacts with two others by π-π stacking interactions forming a novel supramolecular column structural motif running along the crystallographic *c* axis. In the crystalline compound $[Cu(dipdap)_2]AQSO_3 \cdot H_2O$, aggregation between two complex cations and two additional anions by π-π stacking interactions is observed, leading to a tetrameric assembly. Furthermore, the three complex compounds $[Cu(L)_2]BF_4$ (L = dmedap, detdap, dipdap) were tested for sensory applications in aqueous buffer solutions in electrochemical studies of the complex immobilized on glassy carbon electrodes.

Introduction

Dipyrido[3,2-*a*:2′,3′-*c*]phenazine[1] (dppz), eilatin[2] (eil) and 1,12-diazaperylene[3] (dap) are 1,10-phenanthroline-based ligands with increased π surface that are called "large-surface" ligands (Scheme 1).[4] Metal complexes of "large-surface" ligands have enormous potential to form metal organic supramolecular assemblies by π-π stacking interactions in solution and in the solid state. In the planar dichloro(dipyridophenazine)platinum(II) complex $[PtCl_2(dppz)]$, both ligand–ligand π-π and platinum–platinum interactions lead to aggregation of this complex in the crystal, forming two infinite stacks.[5] The octahedral mono(eilatin) Ru^{II} and Os^{II} complexes $[M(L\text{-}L)_2(eil)]^{2+}$ (M = Ru, Os; L-L = bipyridyl-type ligands) dimerize by π-π stacking between the eilatin moieties in the solid state and in solution.[6] In all the solid-state structures, a well-defined discrete dimer is observed in which the eilatin surfaces are about 3.4 Å apart, a typical distance for systems held by π-π stacking interactions.[7]



Scheme 1. "Large-surface" phenanthroline-type ligands.

Recently, we have shown that homoleptic octahedral metal complexes of 1,12-diazaperylene are able to form supramolecular assemblies with honeycomb structures by π-π stacking when the complex cation, $[M(dap)_3]^{2+}$ (M = Ni^{II}, Fe^{II}), adopts a C_3 symmetry and the anions are BF_4^- or PF_6^-.[8]

It is well known that copper(I) complexes of 2,9-disubstituted 1,10-phenanthrolines are key building blocks in supramolecular chemistry and therefore they are found in molecular structures, like molecular racks,[9] nanoboxes,[10] knots,[11] nanogrids,[12] wheels[13] and catenanes.[14]. To investigate the potential of tetrahedral 1,12-diazaperylene

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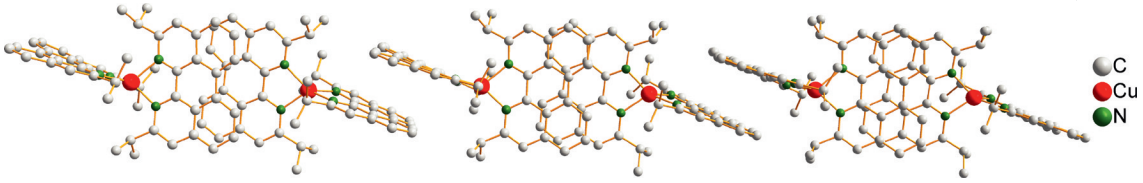
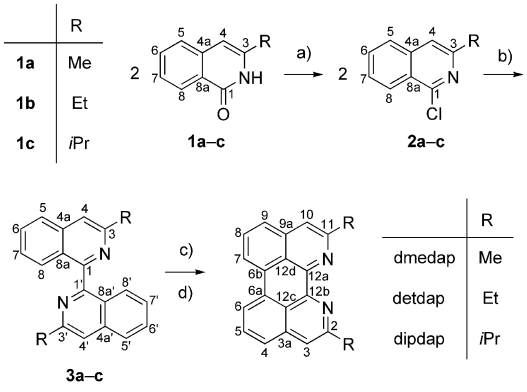


Figure 1. Supramolecular assembly with column structure generated by π-π stacking interaction between tetrahedral copper(I) complex cations in $[Cu(dipdap)_2]BF_4 \cdot CH_2Cl_2 \cdot 1.5H_2O$, viewed along the crystallographic *a* axis. Hydrogen atoms and anions have been omitted for clarity. The solvent molecules CH_2Cl_2 and H_2O are disordered.

complexes for the construction of metal organic supramolecular assemblies by π-π stacking interactions we synthesized 2,11-dialkylated 1,12-diazaperylenes and obtained the first tetrahedral copper(I) complexes of a "large-surface" ligand with these new diazaperylenes. It is well known that in the solid state the coordination geometries of homoleptic tetrahedral copper(I) complexes are strongly influenced by the packing (Figure 1).[15] Therefore, we synthesized 2,11-dialkylated 1,12-diazaperylene with alkyl substituents, which impose different steric hindrance on the arrangement of the partners in the complex [methyl (dmedap), ethyl (detdap) and isopropyl (dipdap), Scheme 2]. Moreover, the copper(I) complexes were prepared with counteranions of different size and shape [BF_4^-, $CF_3SO_3^-$, I^- and $AQSO_3^-$ (9,10-dihydro-9,10-dioxo-2-anthracenesulfonate)]. In the solid state of $[Cu(dipdap)_2]BF_4$, each copper(I) complex cation interacts with two others by π-π stacking interactions, forming an unprecedented supramolecular column assembly. The new copper(I) complexes show low-energy MLCT absorptions yet unparalleled by bis(α-diimin)copper(I) complexes.



Scheme 2. Synthesis of 2,11-dialkylated 1,12-diazaperylenes dmedap, detdap and dipdap. Reagents and conditions: (a) $POCl_3$, reflux; (b) $NiCl_2 \cdot 6H_2O$, TPP, Zn, DMF, 50 °C; (c) K, DME, r.t.; (d) O_2, THF, r.t. TPP = triphenylphosphane, DME = 1,2-dimethoxyethane, r.t. = room temperature.

Results and Discussion

Synthesis of Ligands dmedap, detdap and dipdap

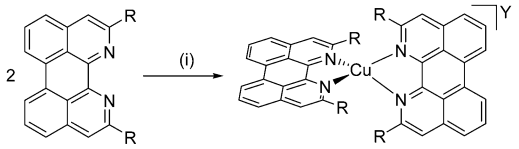
The reaction of an alkyllithium with 1,10-phenanthroline followed by hydrolysis and rearomatization with manganese dioxide gives the 2,9-dialkylated product.[16] This synthetic method is not useful for synthesizing the 2,11-dialkylated derivatives of 1,12-diazaperylene. After workup the unsubstituted dap is completely recovered.

We were successful in preparing dmedap, detdap and dipdap by using 1,1′-biisoquinoline precursors **3a**–**c** bearing the alkyl groups in the desired position. The 3,3′-dialkylated 1,1′-biisoquinolines **3a**–**c** were converted into the corresponding disubstituted dap by a reductive cyclization with potassium following the protocol of Schmelz et al. for synthesizing the unsubstituted dap.[3] Thereby, at first the 1,1′-biisoquinoline is reduced to a dianion, which is then oxidized by air oxygen. We found that by realizing the oxidation under high dilution conditions (10 mmol L^{-1}) the yields could be increased up to 74%.

3,3′-Dimethyl-1,1′-biisoquinoline (**3a**) was prepared after a modified procedure given by Falk and Suste[17] and the unknown 3,3′-dialkyl-1,1′-biisoquinolines **3b**,**c** were synthesized by homocoupling of the corresponding 3-alkyl-1-chloroisoquinolines. The compound **2b** was obtained by a modified method given by Lerch and Granzer[18] and the unknown 1-chloro-3-isopropylisoquinoline **2c** is available from the 3-isopropylisoquinolin-1(2*H*)-one[19] (**1c**) by chlorination with $POCl_3$.

Synthesis and Crystal Structures of Copper(I) Complexes

The copper(I) tetrafluoroborate complexes $[Cu(L)_2]BF_4$ (L = dmedap, detdap, dipdap) were synthesized by the reaction of the ligands with $CuCl_2 \cdot 2H_2O$, followed by reduction with sodium ascorbate and precipitation of the complexes with $NaBF_4$ (Scheme 3, Figure 2). The corresponding triflate salts were obtained by using $Cu(OTf)_2$ as the copper(II) precursor. The bis(2,11-diisopropyl-1,12-diazaperylene)copper(I) complex was also synthesized with iodide and 9,10-dihydro-9,10-dioxo-2-anthracenesulfonate as counterions, yielding the salts $[Cu(dipdap)_2]I$ and $[Cu(dipdap)_2]AQSO_3$, respectively. The new complexes were characterized by elemental analysis and ESI-MS and show a typical green colour. The ^1H and ^{13}C NMR spectra of the complexes in $C_2Cl_4D_2$ show only a quarter signal set, indicating D_{2d} symmetry in solution. Crystalline material suitable for X-ray crystallographic analyses were obtained from the complex compounds $[Cu(dipdap)_2]BF_4$, $[Cu(dipdap)_2]OTf$, $[Cu(dipdap)_2]I$, $[Cu(dmedap)_2]OTf$ and $[Cu(dipdap)_2]AQSO_3$.



R = Me, Et, *i*Pr
Y = BF_4, OTf, I, $AQSO_3$

Compound	Selected reaction conditions (i)	
	Ligand	Copper salt, reducing agent, precipitating reagent
$[Cu(dmedap)_2]BF_4$	dmedap	$CuCl_2·2H_2O$, sodium ascorbate, $NaBF_4$
$[Cu(detdap)_2]BF_4$	detdap	$CuCl_2·2H_2O$, sodium ascorbate, $NaBF_4$
$[Cu(dipdap)_2]BF_4$	dipdap	$CuCl_2·2H_2O$, sodium ascorbate, $NaBF_4$
$[Cu(dmedap)_2]OTf$	dmedap	$Cu(OTf)_2$, sodium ascorbate
$[Cu(detdap)_2]OTf$	detdap	$Cu(OTf)_2$, sodium ascorbate
$[Cu(dipdap)_2]OTf$	dipdap	$Cu(OTf)_2$, sodium ascorbate
$[Cu(dipdap)_2]I$	dipdap	CuI
$[Cu(dipdap)_2]AQSO_3$	dipdap	$CuCl_2·2H_2O$, sodium ascorbate, $NaAQSO_3$ [a]

Scheme 3. Synthesis of copper(I) complexes $[Cu(dmedap)_2]^+$, $[Cu(detdap)_2]^+$ and $[Cu(dipdap)_2]^+$ with different anions. [a] $NaAQSO_3$ = sodium 9,10-dihydro-9,10-dioxo-2-anthracenesulfonate.

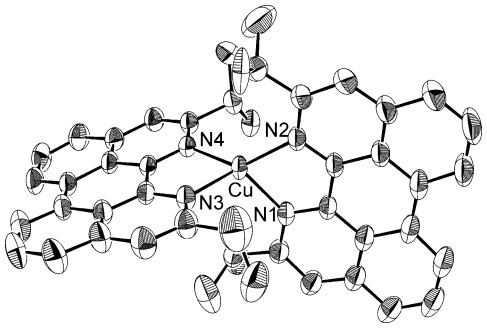


Figure 2. Crystal structure of complex cation $[Cu(dipdap)_2]^+$ in $[Cu(dipdap)_2]BF_4·CH_2Cl_2·1.5H_2O$ with 50% ellipsoids. Hydrogen atoms have been omitted for clarity.

Selected structural data are given in Table 1 and the crystal data and collected parameters are listed in Tables S1–S2 (Supporting Information). In the solid-state structure of $[Cu(dipdap)_2]BF_4·CH_2Cl_2·1.5H_2O$, the complex cation $[Cu(dipdap)_2]^+$ shows a distorted tetrahedral coordination geometry (Figure 1). In $[Cu(dipdap)_2]BF_4·CH_2Cl_2·1.5H_2O$, each copper(I) complex cation interacts with two others by π-π stacking interactions, forming an unprecedented supramolecular column structural motif running along the crystallographic *c* axis (Figure 1). The BF_4^- counterion is located between the columns (Figure 3). All five arene rings of each 2,11-diisopropyl-1,12-diazaperylene (dipdap) are involved in the π-π stacking interactions between two dipdap ligands of two complex cations. They interact in a parallel-displaced mode.[7] The centroid–centroid distances and displacement angles are in the ranges of 3.74–3.83 Å and 22.4–25.3°, respectively. The distance between the two approximately parallel planes that separate the two dipdap ligands is 3.459 Å. However, up to now we observed the formation of a columnar structure by π-π stacking only in the case of $[Cu(dipdap)_2]BF_4·CH_2Cl_2·1.5H_2O$. Using the anion OTf^- instead of BF_4^- in CH_2Cl_2, the complex cation $[Cu(dipdap)_2]^+$ crystallizes as $[Cu(dipdap)_2]OTf·CH_2Cl_2$ in discrete dimers of $[Cu(dipdap)_2]^+$, held together by π-π stacking (Figure 4).

The mode of π-π stacking interactions between two dipdap ligands in $[Cu(dipdap)_2]OTf·CH_2Cl_2$ resembles that found in $[Cu(dipdap)_2]BF_4·CH_2Cl_2·1.5H_2O$. All five arene rings of each dipdap ligand are involved in the π-π stacking aggregation. The distance between the two interacting dipdap ligands is 3.38 Å. This is shorter than that in the column structure, reflecting the stronger π-π interaction in the dimer structure. If iodide is used as the counterion for $[Cu(dipdap)_2]^+$, as in the crystalline compound $[Cu(dipdap)_2]I·C_2H_4Cl_2·THF·2H_2O$, no π-π stacking aggregation can be observed. We assume that in comparison to BF_4^- and $CF_3SO_3^-$ the I^- anion prevents π-π stacking interaction between the complex cations $[Cu(dipdap)_2]^+$. $[Cu(dmedap)_2]OTf$ was obtained from dmedap and $Cu(OTf)_2$

Table 1. Selected structural data for $[Cu(dipdap)_2]^+$ and $[Cu(dmedap)_2]^+$ complexes.

	$[Cu(dipdap)_2]$-$BF_4·CH_2Cl_2·1.5H_2O$	$[Cu(dipdap)_2]$-$OTf·CH_2Cl_2$	$[Cu(dipdap)_2]I·C_2H_4Cl_2·THF·2H_2O$	$[Cu(dmedap)_2]$-$OTf·C_2H_4Cl_2$	$[Cu(dipdap)_2]$-$AQSO_3·H_2O$
Cu1–N1 [Å]	2.029(2)	2.033(2)	2.032(4)	2.025(2)	2.026(3)
Cu1–N2 [Å]	2.067(2)	2.046(2)	2.033(4)	2.028(2)	2.047(3)
Cu1–N3 [Å]	2.042(2)	2.044(2)	2.032(4)	2.018(2)	2.054(3)
Cu1–N4 [Å]	2.068(2)	2.037(2)	2.033(4)	2.033(2)	2.031(3)
N1–Cu–N2 [°]	81.7(2)	82.2(2)	82.4(2)	81.8 (1)	82.8(2)
N3–Cu–N4 [°]	81.7(2)	81.9(2)	82.4(2)	82.1(2)	82.6(2)
N1–Cu–N4 [°]	124.7(1)	132.3(1)	129.2(2)	126.2(2)	131.8(2)
N2–Cu–N3 [°]	122.4(1)	119.0(2)	128.9(2)	133.4(1)	121.1(2)
N4–Cu–N2 [°]	113.3(2)	118.9(2)	120.2(2)	114.1(2)	120.1(2)
N1–Cu–N3 [°]	136.5(2)	126.5(1)	120.2(2)	125.1(1)	123.6(2)
Distortion around Cu[a]					
θ_x [°]	98.6	87.7	89.9	97.4	86.7
θ_y [°]	100.6	98.2	90.1	92.0	95.8
θ_z [°]	88.9	87.2	81.6	80.0	86.1
Cu displ. from ligand plane [Å]	0.249 0.228	0.046 0.021	0.046 0.046	0.056 0.025	0.187 0.142

[a] The distortion around the copper(I) can be described by θ_x, θ_y and θ_z, as shown in Figure 7.

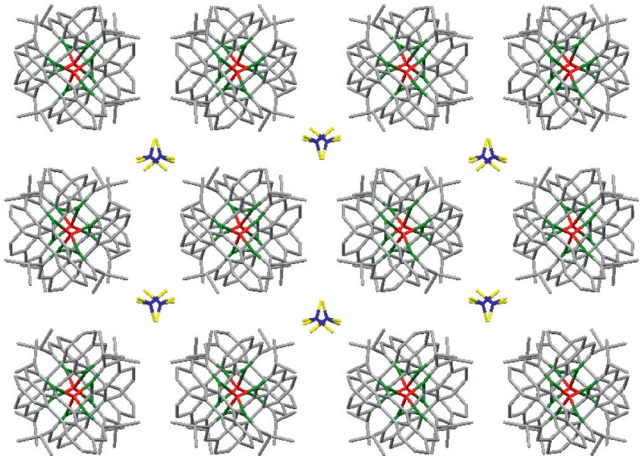


Figure 3. Column structure of $[Cu(dipdap)_2]BF_4 \cdot CH_2Cl_2 \cdot 1.5H_2O$, view down *c*; the BF_4^- counterions are located between the columns. Cu (red); N (green), C (grey), B (blue), F (yellow). Hydrogen atoms have been omitted for clarity. The solvent molecules CH_2Cl_2 and H_2O are disordered.

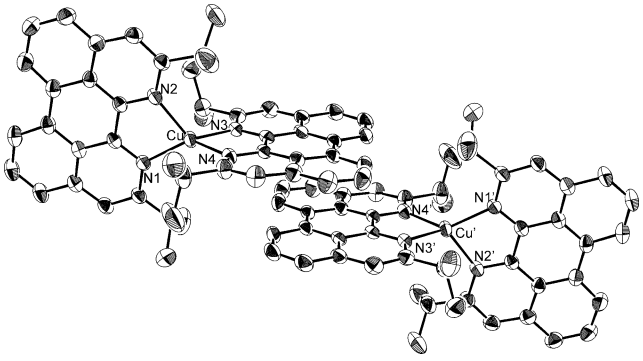


Figure 4. Dimer formation in $[Cu(dipdap)_2]OTf \cdot CH_2Cl_2$ by π-π stacking between two complex cations. Hydrogen atoms, anions and solvent molecules have been omitted for clarity.

and sodium ascorbate as the reducing agent. In 1,2-dichloroethane, $[Cu(dmedap)_2]OTf$ crystallizes with one solvent molecule. X-ray analysis revealed that in this solid structure the complex cation $[Cu(dmedap)_2]^+$ forms dimers by π-π stacking interactions (Figure 5), as previously observed for the dipdap complex in $[Cu(dipdap)_2]OTf \cdot CH_2Cl_2$. These results suggest that the influence of the alkyl substituents of the 2,11-dialkylated 1,12-diazaperylenes on the π-π stacking properties of the corresponding copper(I) complexes is considerably small. In contrast, our studies lead to the conclusion that the counterion has a more pronounced influence on the π-π stacking properties. Unfortunately, up to now crystals of $[Cu(dmedap)_2]BF_4$ have not been accessible. Based on the aforementioned structural features, this compound should also form a columnar structure by π-π stacking, comparable with $[Cu(dipdap)_2]BF_4$. Being able to tune the π-π stacking-mediated supramolecular inorganic chemistry of metal complex cations of "large-surface" ligands simply by choice of the counterion would offer a wealth of opportunities in system design, especially as the anion does not have to be a small inorganic one (e.g., I^-), but could also be a species that can take part in the π-π interactions, for instance, a negatively charged aromatic organic molecule or a negatively charged metal complex of a "large-surface" ligand. To get an idea of such integrative π stacking models, we synthesized the compound $[Cu(dipdap)_2]AQSO_3$ in which the anion is 9,10-anthrachinone-2-sulfonate ($AQSO_3$). In the crystalline compound $[Cu(dipdap)_2]AQSO_3 \cdot H_2O$, a π-π stacking-induced tetrameric assembly of two complex cations $[Cu(dipdap)_2]^+$ and two additional $AQSO_3$ anions was observed (Figure 6). The distance between the two approximately parallel planes that separate the coordinated dipdap and the anion $AQSO_3$ is relatively long for π-π stacking interactions, amounting to 3.7 Å. The corresponding distance between both dipdap ligands is shorter (3.5 Å).

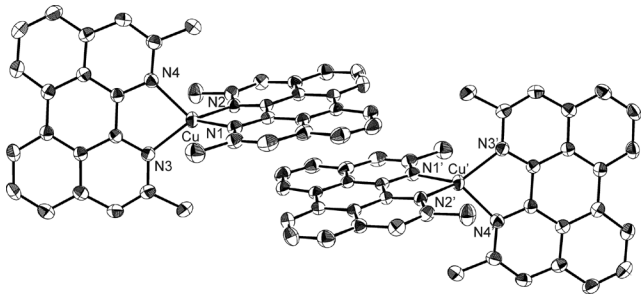


Figure 5. Dimer formation in $[Cu(dmedap)_2]OTf \cdot C_2H_4Cl_2$ by π-π stacking between two complex cations. Hydrogen atoms, anions and solvent molecules have been omitted for clarity.

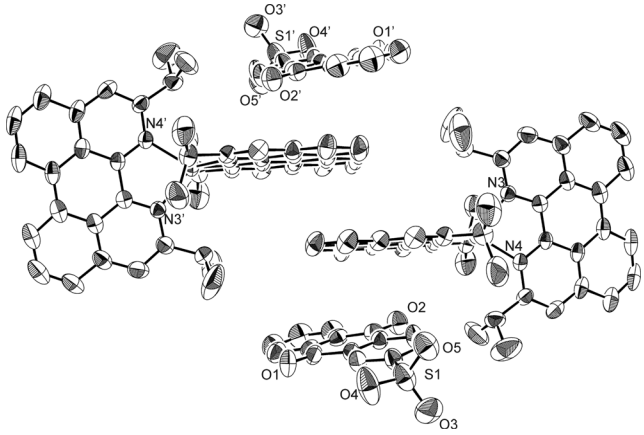


Figure 6. Tetrameric assembly in $[Cu(dipdap)_2]AQSO_3 \cdot H_2O$ generated by π-π stacking between two complex cations $[Cu(dipdap)_2]^+$ and two additional $AQSO_3$ anions. Hydrogen atoms and water molecules have been omitted for clarity.

In the solid state, all copper(I) complexes characterized by X-ray crystallographic analysis show a distorted tetrahedral coordination geometry, which is different for each compound. A measure for the deviation from the idealized tetrahedral coordination geometry is the degree of the rocking and flattening distortion. Flattening distorts the molecules from an idealized tetrahedral geometry to a square-planar geometry and a rocking distortion results in one longer Cu–N bond and a pyramidal coordination geometry. Coppens and co-workers[20] showed that these distortions can easily

be induced by relatively weak intermolecular forces. The distortion around the copper centre can be described by the θ_x, θ_y and θ_z angles, as defined by White and co-workers (Figure 7).[21] In homoleptic copper(I) complexes, such as those discussed here, θ_x and θ_y are interchangeable and describe the rocking distortions, whereas θ_z corresponds to the flattening. For an idealized tetrahedral geometry all three angles would amount to 90°.

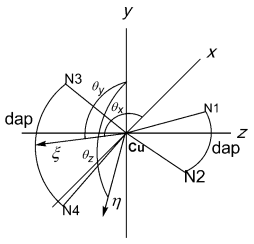


Figure 7. Schematic representation of the distortion around the copper centre in $[Cu(L)_2]^+$ (L = dmedap, detdap, dipdap). The coordinate system is chosen so that the triangle N1–Cu–N2 lies in the *xz* plane. Unit vector ξ bisects the angle N3–Cu–N4 and unit vector η is perpendicular to the triangle N3–Cu–N4. θ_x [°] is the angle between ξ and *X*. θ_y [°] is the angle between ξ and *Y*. θ_z [°] is the angle between η and *y*.

$[Cu(dipdap)_2]I$ shows a higher symmetry than all the other complexes. The asymmetric unit contains only one half of the complex molecule. Interestingly, the tetrahedral complex cation $[Cu(dipdap)_2]^+$ in $[Cu(dipdap)_2]I$ shows a distortion that is significantly different from $[Cu(dipdap)_2]Y$ (Y = BF_4, OTf). This complex has only a flattening distortion of 8.4° (θ_z = 81.6°) and nearly no rocking distortion (θ_x = 89.9°, θ_y = 90.1°). On the other hand, all the other $[Cu(dipdap)_2]^+$ complexes show a small flattening distortion in the range of 1.1° ($[Cu(dipdap)_2]BF_4$) to 3.9° ($[Cu(dipdap)_2]AQSO_3$) and a pronounced rocking distortion of 8.6° (θ_x = 98.6°) and 10.6° (θ_y = 100.6°) in $[Cu(dipdap)_2]BF_4$. These results reveal that not only repulsive interactions between the alkyl substituents of the opposite ligands are crucial for the flattening distortion. The substituent effect can be better assessed when complexes with the same anion such as $[Cu(dipdap)_2]$OTf and $[Cu(dmedap)_2]$OTf are compared. Figures 4 and 5 show that these two species not only have the same anion, but also form similar dimers by π-π stacking interactions in the crystal. The decisive difference between the virtually identical solid-state structures lies in the distortion from the idealized tetrahedral coordination geometry. Whereas $[Cu(dmedap)_2]$OTf has a strong flattening distortion of 10° (θ_z = 80°), $[Cu(dipdap)_2]$OTf shows a negligible flattening distortion of 2.8° (θ_z = 87.2°). This example shows that the introduction of bulky isopropyl groups can generate a small flattening distortion, preventing a square-planar coordination geometry.

In $[Cu(dmedap)_2]^+$ or $[Cu(dipdap)_2]^+$ compounds, the copper atom is generally displaced from both diazaperylene ligand planes, but the correlation with the rocking distortion is not as pronounced as for the known $[Cu(dmephen)_2]^+$ complexes.[20,22] Although $[Cu(dipdap)_2]$OTf shows the second largest rocking distortion, the copper displacement is negligible and is comparable with the iodide complex for which no rocking distortion was found.

Photophysical Properties

Electronic Absorption Spectra

The absorption spectra of the 2,11-dialkylated 1,12-diazaperylenes dmedap, detdap, dipdap and dap are depicted in Figure 8. They show the typical π-π* transitions centred on the perylene chromophore. Substitution with two alkyl groups causes redshifts of the absorption maxima of up to 12 nm compared with dap, conceivable with the inductive effect exerted on the chromophore's π system by introduction of the alkyl groups. Variation of the alkyl group has a negligible effect on the absorption maximum, the slight trend being obvious from the data in Table 2, reflecting the slight difference in Hammett constants of the methyl, ethyl and isopropyl groups.[23]

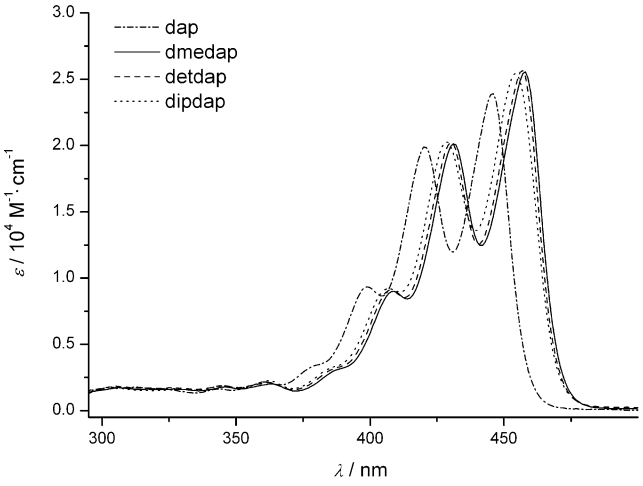


Figure 8. UV/Vis absorption spectra of the ligands in CH_2Cl_2.

Table 2. Absorption data for dmedap, detdap, dipdap and dap. Molar absorption coefficients given in parentheses. Measured in CH_2Cl_2 at r.t.

Ligand	Absorption maxima λ_{max} [nm] (ε, 10^4 M^{-1} cm^{-1})
dap	375 (0.3), 399 (0.9), 420 (2.0), 446 (2.4)
dmedap	386 (0.3), 409 (0.9), 431 (2.0), 458 (2.6)
detdap	384 (0.3), 409 (0.9), 429 (2.0), 457 (2.6)
dipdap	386 (0.3), 407 (0.9), 429 (2.0), 454 (2.5)

Since the studies of Sundararajan and Wehry in the 1970s it has been known that the copper(I) complex $[Cu(dmephen)_2]^+$ can be prepared from 2,9-dimethyl-1,10-phenanthroline (dmephen) and copper(II) chloride in methanol solution by photoreduction of the initially formed five-coordinate copper(II) complex $[Cu(dmephen)_2MeOH]^{2+}$.[24] Here, we could observe the same reaction with 2,11-dialkylated 1,12-diazaperylenes. As an example, Figure 9 shows the absorption spectra of dmedap in the presence of increasing equivalents of copper(II) chloride dihydrate in methanol. It is evident that the typical perylene-centred π-

π* absorption bands of dmedap are hypo- and bathochromically shifted and that new absorption bands appear between 530 and 840 nm. The inset of Figure 9 shows that the linear increase of these bands, with a global maximum at 609 nm, levels off at a molar ratio of dmedap/copper(II) chloride of 2:1, hinting at the complex's stoichiometry. These absorption bands are assigned to MLCT transitions of the tetrahedral copper(I) complex[24] $[Cu(dmedap)_2]^+$ formed by photoreduction of $[Cu(dmedap)_2MeOH]^{2+}$. The UV/Vis spectra of the newly synthesized copper(I) complexes $[Cu(L)_2]BF_4$ (L = dmedap, detdap, dipdap) recorded in dichloromethane are depicted in Figure 10, together with the corresponding spectrum of $[Cu(dmephen)_2]BF_4$. Absorption maxima and molar absorption coefficients are summarized in Table 3.

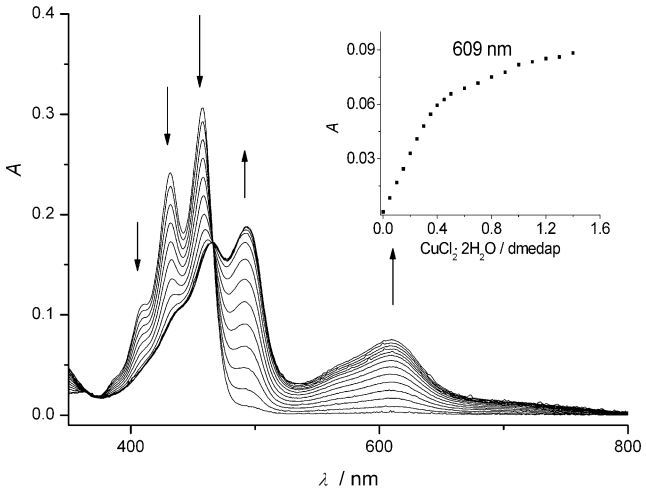


Figure 9. Absorption spectra of dmedap ($c = 2.5 \times 10^{-5}$ M) in the presence of increasing equivalents of copper(II) chloride dihydrate in methanol. Inset: titration curve at 609 nm.

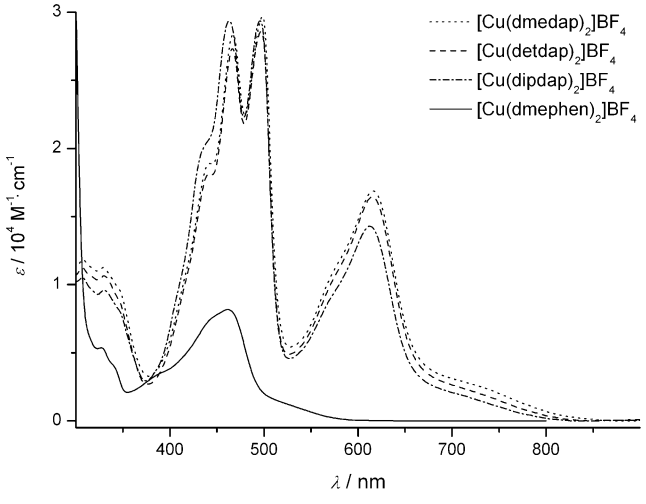


Figure 10. Absorption spectra of the copper(I) complexes recorded in dichloromethane.

Coordination of dmedap, detdap or dipdap to copper(I) induces a bathochromic shift of the ligand-centred π-π* transitions by about 1800 cm^{-1} (compare the respective transitions at about 455 nm in Table 2 with those at about 495 nm in Table 3), which is slightly more pronounced than in the case of dmephen with 1200 cm^{-1} (for the absorption data of dmephen, see ref.[25]), indicating strong complex formation. In the yellow and red visible range of the spectra of complexes $[Cu(L)_2]^+$ (L = dmedap, detdap, dipdap), at least three MLCT bands are found, one above 680 nm, a second one with the global MLCT maximum at about 615 nm and a third one exemplified by a shoulder at about 570 nm. The overall shape of the MLCT absorption bands is typical for comparable homoleptic bis(diimine)copper(I) complexes, for example, $[Cu(dmephen)_2]BF_4$ (Figure 10).[26] However, to the best of our knowledge, the MLCT transitions of complexes $[Cu(L)_2]^+$ (L = dmedap, detdap, dipdap) are the lowest-energy ones that have yet been reported for bis(diimine)copper(I) complexes. Moreover, all three complexes exhibit relatively high molar absorption coefficients for the MLCT transition at about 615 nm ($\varepsilon \approx 17000$ $M^{-1} cm^{-1}$).

Table 3. Absorption data.[a] Molar absorption coefficients given in parentheses.

Complex	Absorption maxima λ_{max} [nm] (ε, 10^4 $M^{-1} cm^{-1}$)
$[Cu(dmephen)_2]BF_4$[b]	327 (0.5), 390 (0.4), 457 (0.8)
$[Cu(dmedap)_2]BF_4$	330 (1.1), 445 sh (1.9), 467 (2.8), 498 (3.0), 616 (1.7)
$[Cu(detdap)_2]BF_4$	330 (1.1), 445 sh (1.8), 467 (2.8), 497 (2.9), 616 (1.7)
$[Cu(dipdap)_2]BF_4$	330 (1.0), 440 sh (2.0), 463 (2.9), 496 (2.9), 612 (1.4)

[a] Recorded in dichloromethane. [b] From ref.[28].

Both results are associated with the extended aromatic π-system of the title ligands in comparison to phenanthroline-type ligands such as dmephen, leading to reduced HOMO–LUMO gaps and enhanced oscillator strengths.[27] Although the absolute value of the global MLCT absorption maximum of $[Cu(dipdap)_2]BF_4$ (612 nm) differs slightly from the values of the other two 2,11-dialkyl-1,12-diazaperylene complexes (616 nm), its displacement with respect to the lowest-energy intraligand band is very similar, amounting to 5650 cm^{-1} for all three complexes. Whereas these energetic results are mainly related to the degree of π delocalization, the reduction of the molar absorption coefficient of $[Cu(dipdap)_2]BF_4$ by about 20% compared with $[Cu(dmedap)_2]BF_4$ and $[Cu(detdap)_2]BF_4$ tentatively reflects the enhanced steric strain in the complex where the ligand carries the sterically more demanding, branched alkyl groups. Earlier studies by McMillin's group on bis(2,9-disubstituted-phenanthroline)copper(I) complexes support our findings. Their work revealed that in $[Cu(L)_2]^+$ complexes with L = 2,9-disubstituted phenanthroline, bulky substituents can interact with the ligand core of the opposite ligand, thereby reducing the conformational freedom of the substituents and entailing an increase in the average metal–ligand separation, which in turn results in a reduced intensity of the MLCT absorption.[28]

Luminescence Measurements

In contrast to the known bis(2,9-dialkyl-1,10-phenanthroline)copper(I) complexes, the bis(2,11-dialkyl-1,12-diazaperylene) copper(I) complexes show no MLCT emission

in dichloromethane or methanol even if cooled to 77 K in EtOH/MeOH (4:1) with the setups employed in our work. In principle, this lack of emission can either have coordinative or energetic reasons. With regard to coordinative saturation at the metal centre, it is known that the luminescence intensity and lifetime depend on the coordination environment in the MLCT excited state. As upon MLCT excitation the metal centre changes its formal oxidation state from Cu^{I} to Cu^{II}, the Franck–Condon-excited MLCT state tends to approach a more flattened coordination geometry. In the flattened structure however a fifth coordination site is made available at the newly formed d^9 ion, allowing for attack by nucleophilic species such as solvent molecules and counterions. Depending on the nature of the bonds and species involved, coordinative bond formation and dissociation is possible, providing a facile path for radiationless deexcitation.[29] In phenanthroline copper(I) complexes, the formation of such nonemissive pentacoordinate exciplexes is prevented by choosing bulky substituents that shield the metal site from intermolecular attack.[30,31] According to this theory, the bulky isopropyl groups of the $[Cu(dipdap)_2]BF_4$ should sufficiently prevent the metal centre from nucleophilic attack. Nonetheless, this complex also does not luminesce. Thus we tend to favour a second, energetic deactivation pathway. The emission of complexes such as $[Cu(dmephen)_2]^+$ is found at about 720 nm, virtually independent of solvent polarity, that is, Stokes shifted for about 8200 cm^{-1} with respect to the MLCT absorption band.[28] Transferring such CT stabilization-induced shifts to the title complexes with a global MLCT absorption maximum at about 615 nm and the low-energy part of the absorption spectrum stretching until >800 nm, the luminescence would be expected at >1000 nm. If we take further into account that phenanthroline-type Cu^{I} complexes already possess low luminescence quantum yields between 10^{-4} and 10^{-3},[29,32] accelerated internal conversion according to the energy gap rule would render species that are emitting even further in the red intrinsically less luminescent.[33] We thus assume that the luminescence of the title complex is so weak and redshifted that it escapes the detection capability of our instruments. Additionally, as is known from heteroleptic Ru^{II} complexes of π-extended ligands such as $[Ru(bpy)_2(dap)]^{2+}$ or $[Ru(bpy)_2(dppz)]^{2+}$,[34] involvement of a close-lying dark state and its coupling with the MLCT state can lead to enhanced quenching.[35] Theoretical calculations for dipyrido[3,2-*a*:2′,3′-*c*]phenazine complexes predict that the dark state can be assigned to a $^3\pi\pi^*$ state centred on the π extended ligand. Because of the low-energy $^1\pi$-π* absorption of diazaperylenes (400–500 nm), a low-lying dark state is not unlikely for complexes possessing diazaperylenes. The lack of emission in the diazaperylene copper(I) complexes is thus most likely connected to the reduced energy gap between excited and ground state, potentially involving coupling with a close-lying nonemissive state.

Electrochemistry

The redox behaviour of the new complexes was studied in dichloromethane and acetonitrile. The low solubility of $[Cu(dmedap)_2]BF_4$ did not allow its electrochemical characterization in acetonitrile. The results are collected in Table 4 together with the data for $[Cu(dmephen)_2]^+$[30] and $[Cu(dipphen)_2]^+$[36] (dipphen = 2,9-diisopropyl-1,10-phenanthroline) obtained under identical conditions. All new complexes display a single reversible copper-centred oxidation($Cu^{I/II}$), as well as several successive one-electron ligand-centred reductions. The complex $[Cu(dmedap)_2]^+$ is oxidized in CH_2Cl_2 at 0.93 V versus SCE, which is very similar to the corresponding phenanthroline complex $[Cu(dmephen)_2]^+$.[30] This indicates that the metal d orbitals of copper(I) are not strongly influenced by complexation with 2,11-dialkylated 1,12-diazaperylene compared with phenanthroline. The oxidation potentials of the copper centres in $[Cu(dipdap)_2]^+$ and $[Cu(detdap)_2]^+$ are anodically shifted with respect to that of $[Cu(dmedap)_2]^+$ (1.03 V and 1.09 V compared to 0.93 V vs. SCE in CH_2Cl_2, respectively). The same trend was observed for the phenanthroline analogues. Cunningham and McMillin[36] explore these results with the idea that bulky alkyl substituents in the 2,9-position of phenanthroline favour a tetrahedral coordination geometry and preferentially stabilize the copper(I) oxidation state. The first and second reversible one-electron waves appearing around –0.97 V and –1.23 V in CH_2Cl_2, respectively, are attributed to two consecutive reductions of the 2,11-dialkylated 1,12-diazaperylene, consistent with their low-lying π* orbitals in comparison to the phenanthroline ligands. As has already been observed for phenanthroline copper(I) complexes,[30] the oxidation potentials substantially depend on the solvent.

Table 4. Half-wave potentials for the oxidation and reduction of the complexes.[a]

Complex	$Cu^{I/II}$		E_{red1}		E_{red2}	
	CH_2Cl_2	CH_3CN	CH_2Cl_2	CH_3CN	CH_2Cl_2	CH_3CN
$[Cu(dmephen)_2]^+$[b]	+0.93 (97)	+0.77 (72)	–	–1.72 (65)	–	–
$[Cu(dipphen)_2]^+$[c]	+1.05 (80)	+0.89 (60)	–	–1.81 (50)	–	–
$[Cu(dmedap)_2]^+$	+0.93 (94)	–[d]	–0.97 (118)	–[d]	–1.22[e]	–[d]
$[Cu(detdap)_2]^+$	+1.03 (82)	+0.85[e]	–0.97 (96)	–0.91[e]	–1.24 (102)	–1.12[e]
$[Cu(dipdap)_2]^+$	+1.09 (80)	+0.94 (84)	–0.98 (64)	–0.92 (88)	–1.24 (89)	–1.10 (63)

[a] Potentials are given in volts vs. SCE (internal standard Fc/Fc^+) in dichloromethane and acetonitrile, with 0.1 M nBu_4PF_6 as the supporting electrolyte, measured at room temperature with a scan rate of 0.2 Vs^{-1}. ΔE_p values [mV] are given in parentheses. [b] From ref.[30]. [c] From ref.[36]. [d] The low solubility of $[Cu(dmedap)_2]BF_4$ did not allow its electrochemical characterization in acetonitrile. [e] Irreversible, measured with DPV.

Electrochemical Studies of Immobilized Complexes in Aqueous Buffer

In order to test the three 2,11-dialkylated 1,12-diazaperylene copper(I) complexes for sensory applications it was necessary to immobilize the complexes on an electrode surface. Because of the hydrophobic character of the ligands, fixation can be easily achieved by deposition out of an aqueous acetone solution after evaporation of the solvent. Preferential adsorption was found at glassy carbon electrodes (GCE). A layer was formed on the electrodes which turned out to be stable in an aqueous solution (at least for several days).

The electrochemical properties have been determined by cyclic voltammetry. The absorbed complexes showed clearly developed redox peaks for oxidation and reduction. This is illustrated in Figure 11 with $[Cu(dipdap)_2]BF_4$ as an example. The formal potentials of the different complexes are summarized in Table 5. The values are quite close to each other but differ from immobilized copper(I) complex $[Cu(dmephen)_2]BF_4$ (+385 mV vs. Ag/AgCl). Electrochemical measurements of the three new copper(I) complexes in an organic solvent showed much more pronounced differences. Thus, it can be concluded that the interaction with the surface at the interface between electrode and aqueous solution results in a rather similar redox environment for the central copper ion without dissociation of the immobilized complex. The electroactive surface concentration of the complexes was found to be between 200 pmol cm^{-2} for the 2,11-diethyl- and 1300 pmol cm^{-2} for the 2,11-dimethyl-1,12-diazaperylene copper(I) complex.

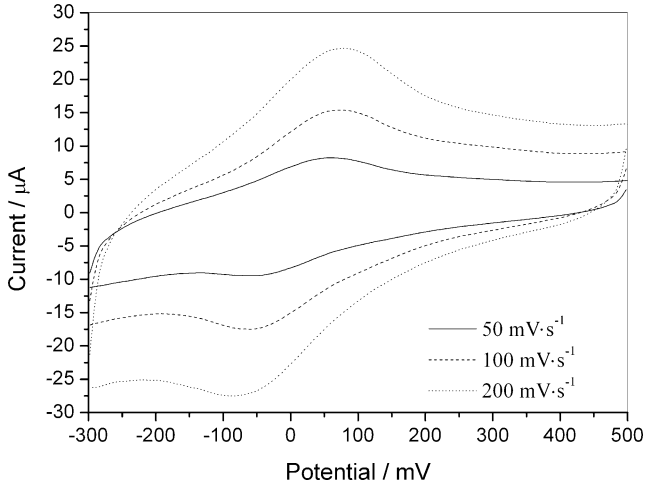


Figure 11. Cyclic voltammograms of $[Cu(dipdap)_2]^+$ absorbed onto glassy carbon electrodes for different scan rates. Conditions: NaPP 0.1 M (pH 7.0), reference Ag/AgCl/1 M KCl.

The kinetics of the redox conversion were also analysed and could be described by the model of Laviron,[37] which allowed determination of the heterogeneous electron transfer constant k_s, the transfer coefficient α and the surface concentration Γ. For all complexes, an α value of 0.5 was found. The electron transfer rate for $[Cu(dmedap)_2]BF_4$ on glassy carbon is slightly higher than for $[Cu(dipdap)_2]BF_4$ but much higher than for $[Cu(detdap)_2]BF_4$. However, for all the immobilized complexes, the electron transfer is quasireversible, which can be considered as a prerequisite for use in sensory applications. Current work in this direction is in progress.

Table 5. Formal potential E_f [mV], peak separation ΔE_p [mV], heterogeneous electron transfer constant k_s [s^{-1}], transfer coefficient α and surface concentration Γ [mol cm^{-2}] of the different bis(2,11-dialkyl-1,12-diazaperylene)copper(I) tetrafluoroborate complexes on a GCE in buffer (pH 7.0).

Complex	E_f	ΔE_p [100 mV s^{-1}]	k_s	α	Γ
$[Cu(dmedap)_2]BF_4$	–3	108	13.0	0.5	1.30×10^{-9}
$[Cu(detdap)_2]BF_4$	+1	105	32.2	0.5	0.20×10^{-9}
$[Cu(dipdap)_2]BF_4$	–8	102	15.4	0.5	0.37×10^{-9}

Conclusions

In summary, we have shown that the newly synthesized 2,11-dialkylated 1,12-diazaperylene ligands are able to form "large-surface" copper(I) complexes, resulting in unique supramolecular column assemblies governed by π-π stacking interactions. At present, we are synthesizing tetrahedral zinc(II) complexes of the 2,11-dialkylated 1,12-diazaperylenes with the aim to broaden the application-oriented features of such "large-surface" supramolecular complex motifs through intercomplex π-π stacking and exciton generation in the solid-state structures. Moreover, 2,11-dialklated 1,12-diazaperylenes are potentially useful ligands for obtaining solid-state π-stacked spin crossover complexes. Such structures and their supramolecular interactions could result in systems showing information transport at a molecular level.

With the results of this and earlier works,[8] we have shown that the dimensionality of the π-π stacking interactions between metal complexes of 1,12-diazaperylenes or 2,11-dialkylated 1,12-diazaperylenes is a function of the coordination geometry. Whereas homoleptic octahedral metal complexes of 1,12-diazaperylenes form a supramolecular 3D honeycomb structure, homoleptic tetrahedral complexes could form 1D columnar structures. As π-π stacking between metal complexes involves strong electronic coupling, the combination of such electronic coupling with supramolecular complex ensembles of different dimensionality and different metal ions promises to be a versatile strategy to create new materials with exciting properties.

Experimental Section

General: All reactions were carried out in dry solvents under argon or nitrogen. 3-Alkylisoquinolin-1(2*H*)-ones were prepared according to known procedures.[19] The reference complex $[Cu(dmephen)_2]BF_4$ was synthesized following the methods described for $[Cu(dmedap)_2]BF_4$. NMR spectra were recorded with an Avance 300 spectrometer. IR spectra were recorded with a Thermo Nicolet NEXUS FTIR instrument. UV/Vis measurements were carried out

with a Perkin–Elmer UV/Vis Spectrometer Lambda 2 using sealed quartz cuvettes. The ESI spectra were recorded using a Micromass Q-TOF$_{micro}$ mass spectrometer in positive electrospray mode. Elemental analyses (C,H,Cl,N,S) were performed with an Elementar Vario EL elemental analyzer. For room-temperature luminescence measurements, a Spectronics Instrument 8100 spectrofluorometer with T-optics configuration was employed, allowing for the detection of luminescence in the wavelength ranges 300–750 and 650–1100 nm. Luminescence measurements at 77 K were performed with a Perkin–Elmer LS50B fluorometer equipped with a low-temperature accessory unit (detection range 250–850 nm). Solutions adjusted to optical densities of 0.05, 0.1 and 0.3 at the MLCT absorption maximum were employed. Electrochemical measurements were performed with a BAS 100B system using a glassy carbon electrode as working electrode, a platinum wire as auxiliary electrode and a $Ag/AgNO_3$ electrode as working electrode. The experiments were conducted in degassed CH_3CN solutions using 0.1 M $[nBu_4N][PF_6]$ as the supporting electrolyte and the ferrocene/ferrocinium (Fc/Fc^+) couple as a reference.

CCDC-723847 (for $[Cu(dipdap)_2]BF_4{\cdot}CH_2Cl_2{\cdot}1.5H_2O$), -723846 (for $[Cu(dmedap)_2]OTf{\cdot}C_2H_4Cl_2$), -723850 (for $[Cu(dipdap)_2]OTf{\cdot}CH_2Cl_2$), -723849 (for $[Cu(dipdap)_2]I{\cdot}C_2H_4Cl_2{\cdot}C_4H_{10}O{\cdot}2H_2O$) and -723848 (for $[Cu(dipdap)_2]AQSO_3{\cdot}H_2O$) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Immobilization of the Complexes on the Electrode Surface: The glassy carbon electrode was dipped into an acetone/water (1:5) solution of the complex (5×10^{-5} M). After evaporation of the acetone the electrode was removed and washed several times with water.

1-Chloro-3-ethylisoquinoline (2b): 3-Ethylisoquinolin-1(2*H*)-one (7 g, 40.4 mmol) followed by phosphorus oxychloride (19 mL, 121 mmol) was added to a 100-mL round-bottomed flask equipped with a reflux condenser. After heating the mixture for two hours, the solution was cooled down in an ice bath and quenched by the cautious addition of ethanol (8 mL) followed by water (40 mL). After the suspension was alkalized by the addition of NaOH (10 N), a water steam distillation was carried out. The distillate was extracted with dichloromethane and the organic phase was dried with Na_2SO_4. Finally, the product was obtained after removal of the solvent; yield 7.1 g (92%). $C_{11}H_{10}ClN$ (191.66): calcd. C 68.94, H 5.26, Cl 18.5, N 7.31; found C 68.89, H 5.35, Cl 18.8, N 7.26. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.23 (d, $^3J_{H,H}$ = 8.4 Hz, 1 H, 5-H), 7.72 (d, $^3J_{H,H}$ = 7.9 Hz, 1 H, 8-H), 7.65 (m, 1 H, 6-H), 7.55 (m, 1 H, 7-H), 7.37 (s, 1 H, 4-H), 2.91 (q, $^3J_{H,H}$ = 7.6 Hz, 2 H, CH_2), 1.36 (t, $^3J_{H,H}$ = 7.6 Hz, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 156.2 (C3), 150.6 (C1), 138.5 (C4a), 130.9 (C6), 127.4 (C8), 126.4 (C5), 126.2 (C8a), 125.2 (C7), 117.2 (C4), 30.6 (CH_2), 13.8 (CH_3) ppm. MS (EI): *m*/*z* (%) = 191 (40) $[M]^+$, 157 (100) $[M - Cl]^+$. IR (NaCl): $\tilde{\nu}$ = 2975 (w, H_2C–H aliphatic), 1628 (s, –C=N– aromatic), 773 (s, C–H aromatic), 553 (s, C–Cl) cm^{-1}.

1-Chloro-3-isopropylisoquinoline (2c): As described above from 3-isopropylisoquinolin-1(2*H*)-one (7.6 g, 40.4 mmol); yield 7.7 g (93%). $C_{12}H_{12}ClN$ (205.69): calcd. C 70.07, H 5.88, Cl 17.24, N 6.81; found C 71.06, H 6.04, Cl 17.2, N 6.77. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.25 (d, $^3J_{H,H}$ = 8.4 Hz, 1 H, 5-H), 7.75 (d, $^3J_{H,H}$ = 8.1 Hz, 1 H, 8-H), 7.67 (m, 1 H, 6-H), 7.57 (m, 1 H, 7-H), 7.4 (s, 1 H, 4-H), 3.16 (sept, $^3J_{H,H}$ = 6.9 Hz, 1 H, CH), 1.37 (d, $^3J_{H,H}$ = 6.9 Hz, 6 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 160.2 (C3), 150.6 (C1), 138.6 (C4a), 130.9 (C6), 127.5 (C8), 126.6 (C5), 126.2 (C8a), 125.3 (C7), 115.7 (C4), 35.6 (CH), 22.4 (CH_3) ppm. MS (EI): *m*/*z* (%) = 205 (45) $[M]^+$, 190 (100) $[M - CH_3]^+$. IR (NaCl): $\tilde{\nu}$ = 2956 (w, H_2C–H aliphatic), 1592 (s, –C=N– aromatic), 757 (s, C–H aromatic), 573 (s, C–Cl) cm^{-1}.

3,3′-Dialkyl-1,1′-biisoquinolines 3a–c: Zinc powder (2 g, 30.6 mmol) was added to a stirred, deep blue solution of nickel(II) chloride hexahydrate ($NiCl_2{\cdot}6H_2O$, 7.27 g, 30.6 mmol) and triphenylphosphane (32.1 g, 122.4 mmol) in dimethylformamide (150 mL) under nitrogen at 50 °C. After 2 h, the colour of the mixture changed to red brown and the corresponding 3-alkyl-1-chloroisoquinoline (30.6 mmol) was added. After stirring overnight at 50 °C, the mixture was poured into dilute ammonia solution and stirred under a stream of air for an additional 30 min until the mixture turned blue. The solid was collected by filtration, dried with $CaCl_2$ and chromatographed through a silica gel column. After large amounts of triphenylphosphane and a small amount of triphenylphosphane oxide, the 3,3′-dialkyl-1,1′-biisoquinolines were obtained.

3,3′-Dimethyl-1,1′-biisoquinoline (3a): As described above from **2a** (5.4 g, 30.6 mmol). Eluent: chloroform/methanol (98:2) (R_f = 0.5). For further purification, the residue was suspended in acetone (10 mL), heated under reflux for 15 min, cooled down to 5 °C and filtered to give the product as a white solid; yield 3.65 g (12.8 mmol), 84%; m.p. 202–203 °C. $C_{20}H_{16}N_2$ (284.36): calcd. C 84.48, H 5.67, N 9.85; found C 84.76, H 5.75, N 9.75. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.81 (d, $^3J_{H,H}$ = 8.3 Hz, 2 H, 5,5′-H), 7.61 (m, 4 H, 4,4′,6,6′-H), 7.53 (m, 2 H, 8,8′-H), 7.33 (m, 2 H, 7,7′-H), 2.79 (s, 6 H, 2 CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 157.8 (C1), 150.8 (C3), 137.5 (C4a), 130.1 (C6), 127.1 (C8), 126.4 (C5), 126.2 (C7), 126.0 (C8a), 119.0 (C4), 24.3 (CH_3) ppm. MS (EI): *m*/*z* (%) = 283 (100) $[M - H]^+$. IR (KBr): $\tilde{\nu}$ = 2919 (w, –H_2C–H aliphatic), 1620 (w, –C=N– aromatic), 749 (s, C–H aromatic), 721 (s, C–H aromatic), 694 (s, C–H aromatic) cm^{-1}.

3,3′-Diethyl-1,1′-biisoquinoline (3b): As described above from **2b** (5.8 g, 30.6 mmol). Eluent: $CHCl_3$ (R_f = 0.5). For further purification, the residue was crystallized from acetone/hexane to give the product as a white solid; yield 2.96 g (9.5 mmol), 62%; m.p. 199–201 °C. $C_{22}H_{20}N_2$ (312.41): calcd. C 84.58, H 6.45, N 8.97; found C 84.65, H 6.53, N 9.03. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.84 (d, $^3J_{H,H}$ = 8.8 Hz, 2 H, 5,5′-H), 7.61 (m, 6 H, 4,4′,6,6′8,8′-H), 7.35 (m, 2 H, 7,7′-H), 3.08 (q, $^3J_{H,H}$ = 7.5 Hz, 4 H, 2 ×-CH_2), 1.44 (t, $^3J_{H,H}$ = 7.5 Hz, 6 H, 2 CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 157.7 (C1), 155.9 (C3), 137.7 (C4a), 130.0 (C6), 127.1 (C8), 126.4 (C5), 126.3 (C7), 126.2 (C8a), 117.5 (C4), 31.1 (CH_2), 14.3 (CH_3) ppm. MS (EI): *m*/*z* (%) = 311 (100) $[M]^+$. IR (KBr): $\tilde{\nu}$ = 2970 (s, –H_2C–H aliphatic), 1586 (s, –C=N– aromatic), 696 (s, C–H aromatic) cm^{-1}.

3,3′-Diisopropyl-1,1′-biisoquinoline (3c): As described above from **2c** (6.3 g, 30.6 mmol). Eluent: CH_2Cl_2 (R_f = 0.6). For further purification, the residue was crystallized from acetone/hexane to give the product as a white solid; yield 3.9 g (11.5 mmol), 75%; m.p. 195–197 °C. $C_{24}H_{22}N_2$ (338.45): calcd. C 85.17, H 6.55, N 8.28; found C 85.18, H 6.63, N 8.35. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.86 (d, $^3J_{H,H}$ = 8.3 Hz, 2 H, 5,5′-H), 7.73 (m, 2 H, 8,8′-H), 7.62 (m, 4 H, 4,4′,6,6′-H), 7.37 (m, 2 H, 7,7′-H), 3.34 (sept, $^3J_{H,H}$ = 6.9 Hz, 2 H, CH), 1.47 (d, $^3J_{H,H}$ = 6.9 Hz, 12 H, 4 CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.7 (C3), 157.5 (C1), 137.8 (C4a), 129.9 (C6), 127.2 (C8), 126.6 (C5), 126.5 (C8a), 126.2 (C7), 115.8 (C4), 36.0 (CH), 22.8 (CH_3) ppm. MS (EI): *m*/*z* (%) = 339 (100) $[M + H]^+$, 323 (50) $[M - CH_3]$. IR (KBr): $\tilde{\nu}$ = 2961 (s, –H_2C–H aliphatic), 1620 (s, –C=N– aromatic), 746 (s, C–H aromatic) cm^{-1}.

2,11-Dialkyl-1,12-diazaperylene (dmedap, detdap, dipdap): In a Schlenk tube under a stream of argon, 3,3′-dialkyl-1,1′-biisoquino-

line (1.5 mmol) was dissolved in dry 1,2-dimethoxyethane (20 mL). Potassium (0.82 g, 21 mmol), which had been separated from its oxide layer and shredded into small pieces, was then added. The intensely coloured blue mixture was stirred at room temperature for 16 h and the remaining potassium removed subsequently under argon. The solution was diluted with dry THF (100 mL) and stirred under a stream of dry air for an additional 4 h. The solvent was evaporated and the residue chromatographed on basic Al_2O_3 to give the 2,11-dialkyl-1,12-diazaperylenes as yellow solids.

2,11-Dimethyl-1,12-diazaperylene (dmedap): As described above from **3a** (426.5 mg, 1.5 mmol). Eluent: THF. After column chromatography, the residue was crystallized from $CHCl_3$; yield 212 mg (0.75 mmol), 50%; m.p. 212–214 °C. $C_{20}H_{14}N_2$ (282.36): calcd. C 85.08, H 5.00, N 9.92; found C 84.97, H 5.12, N 9.95. ^{1}H NMR (300 MHz, $C_2Cl_4D_2$): δ = 8.2 (dd, $^3J_{H,H}$ = 6.0, $^4J_{H,H}$ = 2.4 Hz 2 H, 6,7-H), 7.66 (m, 4 H, 4,5,8,9-H), 7.50 (s, 2 H, 3,10-H), 2.84 (s, 2 H, 2 CH_3) ppm. ^{13}C NMR (75 MHz, $C_2Cl_4D_2$): δ = 153.3 (C12b), 150.1 (C2), 137.8 (C3a), 130.6 (C6a), 130.5 (C5), 126.9 (C4), 123.4 (C12c), 121.4 (C6), 120.5 (C3), 24.8 (CH_3) ppm. MS (EI): *m*/*z* (%) = 282 (100) $[M]^+$. IR (KBr): $\tilde{\nu}$ = 2946 (s, –H_2C–H aliphatic), 1607 (s, –C=N– aromatic), 760 (s, C–H aromatic) cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (ε, M^{-1} cm^{-1}) = 458 (25600), 431 (20100), 409 (9000), 384 (3035), 362 (2010) nm.

2,11-Diethyl-1,12-diazaperylene (detdap): As described above from **3b** (468.6 mg, 1.5 mmol). Eluent: $CHCl_3$. After column chromatography, the residue was crystallized from CH_2Cl_2/hexane; yield 223.5 mg (0.72 mmol), 48%; m.p. 208–209 °C. $C_{22}H_{18}N_2$ (310.4): calcd. C 85.13, H 5.85, N 9.02; found C 85.09, H 5.95, N 9.03. ^{1}H NMR (300 MHz, $C_2Cl_4D_2$): δ = 8.2 (d, $^3J_{H,H}$ = 7.2 Hz, 2 H, 6,7-H), 7.67 (m, 4 H, 4,5,8,9-H), 7.52 (s, 2 H, 3,10-H), 3.19 (q, $^3J_{H,H}$ = 7.6 Hz, 4 H, 2 CH_2), 1.53 (t, $^3J_{H,H}$ = 7.6 Hz, 6 H, 2 CH_3) ppm. ^{13}C NMR (75 MHz, $C_2Cl_4D_2$): δ = 158.6 (C2), 150.2 (C12b), 137.8 (C3a), 130.6 (C6a), 130.4 (C5), 127.0 (C4), 123.7 (C12c), 121.2 (C6), 118.5 (C3), 31.3 (CH_2), 13.8 (CH_3) ppm. MS (EI): *m*/*z* (%) = 310 (100) $[M]^+$. IR (KBr): $\tilde{\nu}$ = 2962 (s, –H_2C–H aliphatic), 1606 (s, –C=N– aromatic), 764 (s, C–H aromatic) cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (ε, M^{-1} cm^{-1}) = 457 (25700), 429 (20200), 409 (9100), 384 (2915), 362 (2100) nm.

2,11-Diisopropyl-1,12-diazaperylene (dipdap): As described above from **3c** (510.7 mg, 1.5 mmol). Eluent: $CHCl_3$. After column chromatography, the residue was crystallized from CH_2Cl_2/hexane; yield 375.7 mg (1.11 mmol), 74%; m.p. 203–205 °C. $C_{24}H_{22}N_2$ (338.45): calcd. C 85.17, H 6.55, N 8.28; found C 85.19, H 6.65, N 8.23. ^{1}H NMR (300 MHz, $C_2Cl_4D_2$): δ = 8.17 (d, $^3J_{H,H}$ = 7.2 Hz, 2 H, 6,7-H), 7.71 (m, 2 H, 4,9-H), 7.63 (m, 2 H, 5,8-H), 7.51 (s, 2 H, 3,10-H), 3.45 (sep, $^3J_{H,H}$ = 6.9 Hz, 2 H, 2 CH), 1.53 (d, $^3J_{H,H}$ = 6.9 Hz, 12 H, 4 CH_3) ppm. ^{13}C NMR (75 MHz, $C_2Cl_4D_2$): δ = 162.7 (C2), 150.2 (C12b), 137.9 (C3a), 130.6 (C6a), 130.1 (C5), 127.2 (C4), 123.8 (C12c), 121.1 (C6), 116.7 (C3), 36.2 (CH), 23.1 (CH_3) ppm. MS (EI): *m*/*z* (%) = 338 (93) $[M]^+$, 323 (100) $[M – CH_3]^+$. IR (KBr): $\tilde{\nu}$ = 2958 (s, –H_2C–H aliphatic), 1606 (s, –C=N– aromatic), 770 (s, C–H aromatic) cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (ε, M^{-1} cm^{-1}) = 454 (25400), 429 (20200), 407 (9200), 384 (3100), 362 (2200) nm.

Bis(2,11-dimethyl-1,12-diazaperylene)copper(I) Tetrafluoroborate ([Cu(dmedap)$_2$]BF$_4$): Under a nitrogen atmosphere, dmedap (141.2 mg, 0.5 mmol) was dissolved in ethanol (20 mL) and a solution of $CuCl_2 \cdot 2H_2O$ (42.6 mg, 0.25 mmol) in water (2 mL) was added. After stirring for 20 min at room temperature, sodium ascorbate (148.6 mg, 0.75 mmol) in ethanol/water (15 mL, 1:1) was added and the reaction mixture turned green. After 1 h, the complex was precipitated by the addition of $NaBF_4$ (167.7 mg, 1.5 mmol) in water (15 mL). The complex was filtered through a sintered glass frit, washed well with water and dried in a vacuum desiccator over $CaCl_2$. For further purification, the complex was dissolved in a minimum amount of acetone, filtered through a G4 sintered glass frit and precipitated by the addition of diethyl ether. After filtration, the product was washed with diethyl ether and obtained as a green solid; yield 151.9 mg (0.21 mmol), 85%; m.p. > 360 °C. $C_{40}H_{28}BCuF_4N_4$ (715.04): calcd. C 67.19, H 3.95, N 7.84; found C 67.16, H 4.02, N 7.87. ^{1}H NMR (300 MHz, $C_2Cl_4D_2$): δ = 8.58 (d, $^3J_{H,H}$ = 7.2 Hz, 2 H, 6,7-H), 8.01 (d, $^3J_{H,H}$ = 8.0 Hz, 2 H, 4, 9-H), 7.95 (t, $^3J_{H,H}$ = 8.0 Hz, 2 H, 5,8-H), 7.86 (s, 2 H, 3,10-H), 2.38 (s, 2 H, 2 CH_3) ppm. ^{13}C NMR (75 MHz, $C_2Cl_4D_2$): δ = 151.1 (C12b), 148.4 (C2), 137.4 (C3a), 132.4 (C4), 130.0 (C6a), 127.2 (C5), 123.5 (C6), 123.4 (C12c), 123.1 (C3), 120.5 (C3), 24.8 (CH_3) ppm. ESI(HR)-MS: (*m*/*z*) calcd. for $[M – BF_4]^+$ ($[C_{40}H_{28}CuN_4]^+$) 627.1610; found 627.1583. IR (KBr): $\tilde{\nu}$ = 2969 (s, –H_2C–H aliphatic), 1590 (s, –C=N– aromatic), 1061 (s, B–F), 780 (s, C–H aromatic) cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (ε, M^{-1} cm^{-1}) = 616 (16900), 498 (29700), 467 (28400), 445 (18800), 333 (11000) nm.

Bis(2,11-diethyl-1,12-diazaperylene)copper(I) Tetrafluoroborate ([Cu(detdap)$_2$]BF$_4$): Under nitrogen, detdap (155.2 mg, 0.5 mmol) was dissolved in a mixture of ethanol/chloroform (2:1, 20 mL) and a solution of $CuCl_2 \cdot 2H_2O$ (42.6 mg, 0.25 mmol) in water (2 mL) was added. After stirring for 20 min at room temperature, sodium ascorbate (148.6 mg, 0.75 mmol) in ethanol/water (30 mL, 3:1) was added and the colour of the reaction mixture turned green. After 1 h, the chloroform was distilled off and $NaBF_4$ (167.7 mg, 1.5 mmol) in water (15 mL) was added. The complex that precipitated was filtered, washed well with water and dried in a vacuum desiccator over $CaCl_2$. For further purification, the complex was dissolved in a minimum amount of acetone, filtered through a G4 sintered glass frit and precipitated by the addition of diethyl ether. After filtration, the product was washed with diethyl ether and obtained as a green solid; yield 157.9 mg (0.205 mmol) 82%; m.p. > 360 °C. $C_{44}H_{36}BCuF_4N_4$ (771.15): calcd. C 68.53, H 4.71, N 7.27; found C 68.50, H 4.81, N 7.22. ^{1}H NMR (300 MHz, $C_2Cl_4D_2$): δ = 8.6 (d, $^3J_{H,H}$ = 6.6 Hz, 2 H, 6,7-H), 8.01 (m, 4 H, 4,5,8,9-H), 7.87 (s, 2 H, 3,10-H), 2.69 (q, $^3J_{H,H}$ = 7.5 Hz, 4 H, 2 CH_2), 1.06 (t, $^3J_{H,H}$ = 7.5 Hz, 6 H, 2 CH_3) ppm. ^{13}C NMR (75 MHz, $C_2Cl_4D_2$): δ = 156.2 (C2), 148.4 (C12b), 137.5 (C3a), 132.4 (C5), 130.1 (C5), 127.4 (C4), 123.5 (C6), 123.3 (C12c), 122.2 (C3), 31.7 (CH_2), 13.2 (CH_3) ppm. ESI(HR)-MS: (*m*/*z*) calcd. for $[M – BF_4]^+$ ($[C_{44}H_{36}CuN_4]^+$) 683.2236; found 683.2211. IR (KBr): $\tilde{\nu}$ = 2968 (s, –H_2C–H aliphatic), 1605 (s, –C=N– aromatic), 1053 (s, B–F), 770 (s, C–H aromatic) cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (ε, M^{-1} cm^{-1}) = 616 (16500), 497 (28600), 467 (27900), 443 (18100), 333 (10500) nm.

Bis(2,11-diisopropyl-1,12-diazaperylene)copper(I) Tetrafluoroborate ([Cu(dipdap)$_2$]BF$_4$): As described above from dipdap (169.2 mg, 0.5 mmol). Crystals were prepared in a stopped NMR tube, in which the complex was dissolved in CD_2Cl_2. After evaporation of the solvent, single crystals suitable for X-ray crystal analyses were obtained; yield 164.8 mg (0.20 mmol), 80%; m.p. > 360 °C. $C_{48}H_{44}BCuF_4N_4$ (827.25): calcd. C 69.96, H 5.36, N 6.77; found C 69.86, H 5.48, N 6.85. ^{1}H NMR (300 MHz, $C_2Cl_4D_2$): δ = 8.59 (dd, $^3J_{H,H}$ = 6.0, $^4J_{H,H}$ = 2.2 Hz 2 H, 6,7-H), 8.00 (m, 4 H, 4,5,8,9-H), 7.85 (s, 2 H, 3,10-H), 3.01 (sep, $^3J_{H,H}$ = 6.8 Hz, 2 H, 2 CH), 1.05 (d, $^3J_{H,H}$ = 6.8 Hz, 12 H, 4 CH_3) ppm. ^{13}C NMR (75 MHz, $C_2Cl_4D_2$): δ = 160.9 (C2), 148.2 (C12b), 137.7 (C3a), 132.3 (C5), 130.1 (C6a), 127.6 (C4), 123.6 (C12c), 123.5 (C6), 120.5 (C3), 37.7 (CH), 22.6 (CH_3) ppm. ESI(HR)-MS: (*m*/*z*) calcd. for $[M – BF_4]^+$ ($[C_{48}H_{44}CuN_4]^+$) 739.2862; found 739.2884. IR (KBr): $\tilde{\nu}$ = 2961

(s, –H_2C–H aliphatic), 1605 (s, –C=N– aromatic), 1061 (s, B–F), 773 (s, C–H aromatic) cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (ε, $M^{-1}cm^{-1}$) = 612 (14300), 496 (29400), 463 (29400), 437 (20200), 332 (9500) nm.

Bis(2,11-diisopropyl-1,12-diazaperylene)copper(I) Triflate ([Cu(dipdap)$_2$]OTf): Under nitrogen, dipdap (169.2 mg, 0.5 mmol) was dissolved in a mixture of ethanol/chloroform (2:1, 20 mL) and a solution of $Cu(OTf)_2$ (90.4 mg, 0.25 mmol) in water (2 mL) was added. After stirring for 20 min at room temperature, sodium ascorbate (148.6 mg, 0.75 mmol) in ethanol/water (30 mL, 3:1) was added and the reaction mixture turned green. After 1 h, the chloroform was distilled off and the complex precipitated, and was filtered, washed well with water and dried in a vacuum desiccator over $CaCl_2$. Crystals were prepared by diethyl ether vapour diffusion into a dichloroethane solution of the copper complex; yield 173.4 mg (0.2 mmol), 78%; m.p. > 360 °C. $C_{49}H_{44}CuF_3N_4O_3S$ (889.5): calcd. C 66.16, H 4.99, N 6.3, S 3.6; found C 65.86, H 5.08, N 6.37, S 3.8. ^{1}H NMR (300 MHz, $C_2Cl_4D_2$): δ = 8.55 (dd, $^3J_{H,H}$ = 5.7, $^4J_{H,H}$ = 2.4 Hz, 2 H, 6,7-H), 7.98 (m, 4 H, 4,5,8,9-H), 7.83 (s, 2 H, 3,10-H), 3.00 (sep, $^3J_{H,H}$ = 6.8 Hz, 2 H, 2 CH), 1.03 (d, $^3J_{H,H}$ = 6.8 Hz, 12 H, 4 CH_3) ppm. ^{13}C NMR (75 MHz, $C_2Cl_4D_2$): δ = 160.7 (C2), 148.0 (C12b), 137.4 (C3a), 132.2 (C5), 130.0 (C6a), 127.4 (C4), 123.4 (C12c), 123.3 (C6), 120.2 (C3), 37.3 (CH), 22.4 (CH_3) ppm. ESI(HR)-MS: (*m*/*z*) calcd. for [M – O_3SCF_3]$^+$ ([$C_{48}H_{44}CuN_4$]$^+$) 739.2862; found 739.2886. IR (KBr): $\tilde{\nu}$ = 2964 (s, –H_2C–H aliphatic), 1602 (s, –C=N– aromatic), 1277 (s, C–F), 1160 (s, C–F), 1031 (s, C–F), 774 (s, C–H aromatic), 639 (s, C–F) cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (ε, $M^{-1}cm^{-1}$) = 612 (14280), 496 (29375), 463 (29383), 437 (20175), 332 (9474) nm.

Bis(2,11-diisopropyl-1,12-diazaperylene)copper(I) 9,10-Dihydro-9,10-dioxo-2-anthracenesulfonate ([Cu(dipdap)$_2$]AQSO$_3$): Under nitrogen, dipdap (169.2 mg, 0.5 mmol) was dissolved in a mixture of ethanol/chloroform (2:1, 20 mL) and a solution of $CuCl_2 \cdot 2H_2O$ (42.6 mg, 0.25 mmol) in water (2 mL) was added. After stirring for 20 min at room temperature, sodium ascorbate (148.6 mg, 0.75 mmol) in ethanol/water (30 mL, 3:1) was added and the reaction mixture turned green. After 1 h, 9,10-anthraquinone-2-sulfate sodium salt (0.465 mg, 1.5 mmol) in water (5 mL) was added and the chloroform was distilled off. The complex that precipitated was filtered, washed well with water and dried in a vacuum desiccator over $CaCl_2$. Crystals were prepared by diethyl ether vapour diffusion into a dichloroethane solution of the copper complex; yield 192.7 mg (0.19 mmol), 75%; m.p. > 360 °C. $C_{62}H_{51}CuN_4O_5S$ (1027.71): calcd. C 72.46, H 5.00, N 5.45, S 3.12; found C 72.51, H 5.07, N 5.47, S 3.17. ^{1}H NMR (300 MHz, $C_2D_2Cl_4$): δ = 8.76 (s, 0.5 H, 1-H $AQSO_3^-$), 8.56 (dd, $^3J_{H,H}$ = 5.3, $^4J_{H,H}$ = 2.9 Hz, 2 H, 6,7-H), 8.33 (dd, $^3J_{H,H}$ = 8, $^4J_{H,H}$ = 1.3 Hz, 0.5 H, 4-H $AQSO_3^-$), 8.21 (m, 1.5 H, 3,7,6-H $AQSO_3^-$), 7.98 (m, 4 H, 4,5, 8, 9-H), 7.85 (s, 2 H, 3,10-H), 7.73 (m, 1 H, 5,8-H), 3.03 (sep, $^3J_{H,H}$ = 6.9 Hz, 2 H, 2×-CH), 1.06 (d, $^3J_{H,H}$ = 6.9 Hz, 12 H, 4× CH_3) ppm. ^{13}C NMR (75 MHz, $C_2Cl_4D_2$): δ = 182.9 (C9-$AQSO_3^-$), 182.6 (C10-$AQSO_3^-$), 160.9 (C2), 152.9 (C2-$AQSO_3^-$), 148.3 (C12b), 137.7 (C3a), 134.1 (C4a-$AQSO_3^-$), 134.0 (C9a-AQSO3), 133.6 (C8a-$AQSO_3^-$), 133.4 (C5a-$AQSO_3^-$), 133.3 (C3-$AQSO_3^-$), 133.2 (C7-$AQSO_3^-$), 132.3 (C5), 132.1 (C6-$AQSO_3^-$), 130.1 (C6a), 127.6 (C4), 127.2 (C4-$AQSO_3^-$), 127.1 (C8-$AQSO_3^-$), 127.0 (C5-$AQSO_3^-$), 125.5 (C1-$AQSO_3^-$), 123.6 (C12c), 123.5 (C6), 120.5 (C3), 37.7 (CH), 22.7 (CH_3) ppm. ESI(HR)-MS: (*m*/*z*) calcd. for [M – $AQSO_3$]$^+$ ([$C_{48}H_{44}CuN_4$]$^+$) 739.2862; found 739.2888. IR (KBr): $\tilde{\nu}$ = 2958 (s, –H_2C–H aliphatic), 1670 (s, C=O), 1603 (s, –C=N– aromatic), 775 (s, C–H aromatic) cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (ε, $M^{-1}cm^{-1}$) = 612 (14320), 496 (29410), 463 (29395), 437 (20194), 332 (9498) nm.

Bis(2,11-diisopropyl-1,12-diazaperylene)copper(I) Iodide ([Cu(dipdap)$_2$]I): Under nitrogen, dipdap (169.2 mg, 0.5 mmol) was dissolved in a mixture of ethanol/chloroform (2:1, 20 mL) and a suspension of CuI (47.6 mg, 0.25 mmol) in ethanol (10 mL) was added. After stirring for 20 min at room temperature, sodium ascorbate (148.6 mg, 0.75 mmol) in ethanol/water (30 mL, 3:1) was added and the reaction mixture turned green. After 1 h, the chloroform was distilled off and the complex that precipitated was filtered, washed well with water and dried in in vacuo desiccators over $CaCl_2$. Crystals were prepared by diethyl ether vapour diffusion into an acetone solution of the copper complex; yield 110.2 mg (0.13 mmol), 51%; m.p. > 360 °C. $C_{48}H_{44}CuIN_4$ (867.4): calcd. C 66.47, H 5.11, N 6.46; found C 67.53, H 5.06, N 6.8. ^{1}H NMR (300 MHz, $C_2Cl_4D_2$): δ = 8.57 (dd, $^3J_{H,H}$ = 5.8, $^4J_{H,H}$ = 2.5 Hz, 2 H, 6,7-H), 8.12 (m, 4 H, 4,5,8,9-H), 7.85 (s, 2 H, 3,10-H), 3.02 (sep, $^3J_{H,H}$ = 6.9 Hz, 2 H, 2 CH), 1.05 (d, $^3J_{H,H}$ = 6.9 Hz, 12 H, 4 CH_3) ppm. ^{13}C NMR (75 MHz, $C_2Cl_4D_2$): δ = 160.5 (C2), 147.8 (C12b), 137.2 (C3a), 132.0 (C5), 129.8 (C6a), 127.2 (C4), 123.2 (C12c), 123.1 (C6), 120.0 (C3), 37.0 (CH), 22.2 (CH_3) ppm. ESI(HR)-MS: (*m*/*z*) calcd. for [M – I]$^+$ ([$C_{48}H_{44}CuN_4$]$^+$) 739.2862; found 739.2891. IR (KBr): $\tilde{\nu}$ = 2958 (s, –H_2C–H aliphatic), 1605 (s, –C=N– aromatic), 771 (s, C–H aromatic) cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (ε, $M^{-1}cm^{-1}$) = 612 (14366), 496 (29710), 463 (29420), 437 (20210), 332 (9505) nm.

Bis(2,11-dimethyl-1,12-diazaperylene)copper(I) Triflate ([Cu(dmedap)$_2$]OTf): Under nitrogen, dmedap (141.2 mg, 0.5 mmol) was dissolved in ethanol (20 mL) and a solution of $Cu(OTf)_2$ (90.4 mg, 0.25 mmol) in ethanol/water (1:1, 10 mL) was added. After stirring for 20 min at room temperature, sodium ascorbate (148.6 mg, 0.75 mmol) in ethanol/water (15 mL, 1:1) was added and the reaction mixture turned green. The reaction mixture was diluted with water (40 mL) and the solid was separated by filtration. The complex was dried in in vacuo desiccators over $CaCl_2$. Crystals were prepared by diethyl ether vapour diffusion into a dichloroethane solution of the copper complex; yield 163.4 mg (0.21 mmol), 83%; m.p. > 360 °C. $C_{41}H_{28}CuF_3N_4O_3S$ (777.3): calcd. C 63.35, H 3.63, N 7.21, S 4.12; found C 63.7, H 3.42, N 7.16, S 3.98. ^{1}H NMR (300 MHz, $C_2Cl_4D_2$): δ = 8.57 (d, $^3J_{H,H}$ = 7.2 Hz, 2 H, 6,7-H), 8.04 (d, $^3J_{H,H}$ = 8.0 Hz, 2 H, 4, 9-H), 7.97 (t, $^3J_{H,H}$ = 8.0 Hz, 2 H, 5,8-H), 7.85 (s, 2 H, 3,10-H), 2.4 (s, 2 H, 2 CH_3) ppm. ^{13}C NMR (75 MHz, $C_2Cl_4D_2$): δ = 151.3 (C12b), 148.5 (C2), 137.6 (C3a), 132.6 (C4), 130.3 (C6a), 127.4 (C5), 123.7 (C6), 123.6 (C12c), 123.3 (C3), 120.6 (C3), 24.9 (CH_3) ppm. ESI(HR)-MS: (*m*/*z*) calcd. for [M – OTf]$^+$ ([$C_{40}H_{28}CuN_4$]$^+$) 627.1610; found 627.1588. IR (KBr): $\tilde{\nu}$ = 2919 (s, –H_2C–H aliphatic), 1608 (s, –C=N– aromatic), 1275 (s, C–F), 1162 (s, C–F), 1029 (s, C–F), 766 (s, C–H aromatic), 637 (s, C–F) cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (ε, $M^{-1}cm^{-1}$) = 616 (16850), 498 (29720), 467 (28380), 445 (18850), 333 (11300) nm.

Bis(2,11-diethyl-1,12-diazaperylene)copper(I) Triflate ([Cu(detdap)$_2$]OTf): As described for [Cu(dipdap)$_2$]OTf from detdap (155.2 mg, 0.5 mmol); m.p. > 360 °C. $C_{45}H_{36}CuF_3N_4O_3S$ (833.4): calcd. C 64.85, H 4.35, N 6.72, S 3.85; found C 64.77, H 4.42, N 6.36, S 3.75. ^{1}H NMR (300 MHz, $C_2Cl_4D_2$): δ = 8.58 (d, $^3J_{H,H}$ = 6.4 Hz, 2 H, 6,7-H), 7.98 (m, 4 H, 4,5,8,9-H), 7.85 (s, 2 H, 3,10-H), 2.66 (q, $^3J_{H,H}$ = 7.3 Hz, 4 H, 2 CH_2), 1.02 (t, $^3J_{H,H}$ = 7.5 Hz, 6 H, 2 CH_3) ppm. ^{13}C NMR (75 MHz, $C_2Cl_4D_2$): δ = 156.4 (C2), 148.6 (C12b), 137.8 (C3a), 132.5 (C5), 130.3 (C5), 127.6 (C4), 123.8 (C6), 123.4 (C12c), 122.4 (C3), 31.9 (CH_2), 13.4 (CH_3) ppm. ESI(HR)-MS: (*m*/*z*) calcd. for [M – OTf]$^+$ ([$C_{44}H_{36}CuN_4$]$^+$) 683.2236; found 683.2217. IR (KBr): $\tilde{\nu}$ = 2967 (s, –H_2C–H aliphatic), 1604 (s, –C=N– aromatic), 1273 (s, C–F), 1162 (s, C–F), 1031 (s, C–F), 772 (s, C–H aromatic), 637 (s, C–F) cm^{-1}. UV/Vis

(CH_2Cl_2): λ_{max} (ε, $M^{-1}cm^{-1}$) = 616 (16520), 497 (28620), 467 (27930), 443 (18110), 333 (10500) nm.

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