Light from Thin Assemblies

Switching On Luminescence by the Self-Assembly of a Platinum(II) Complex into Gelating Nanofibers and Electroluminescent Films**

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Triplet emitters based on platinum(II) complexes have gained major attention in recent times.[1] They can form aggregates or excimers, causing shifts in the emitted wavelengths and affecting the photoluminescence quantum yields (PLQYs).[2] Even though this effect can be exploited for the construction of white organic light emitting diodes (WOLEDs),[3] it is disadvantageous for applications where color purity is desirable. Terpyridine ligands[4] and their N^C^N and N^N^C analogues[5] have been coordinated to platinum(II), leading to neutral, mono-, or doubly charged species, some of which display bright luminescence. They can form supramolecular structures, such as nanowires, nanosheets, and polymeric mesophases, with interesting optical properties.[6]

For low-molecular-weight organo- or hydrogelators,[7] the operating mechanism of gelation has been recognized as a supramolecular effect, where the constituting fibers, usually of microscale lengths and nanoscale diameters, are formed in solution predominantly by unidirectional self-assembly.[8] The entanglement of 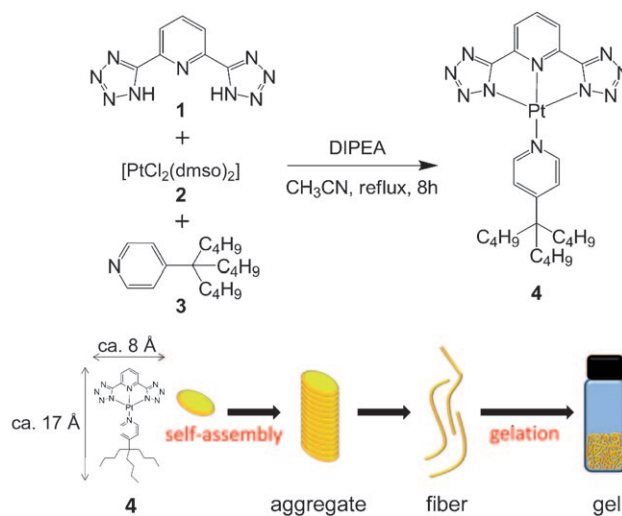filaments gives a network that entraps solvent molecules within the compartments. As supramolecular gels provide fibrous aggregates with long-range order, they could be of interest in the fields of optoelectronic devices and sensors. In this context, organometallic gelators can display metal–metal interactions that influence their properties.[9]

Herein we present a straightforward one-pot synthesis of neutral, soluble platinum(II) coordination compounds bearing a dianionic tridentate terpyridine-like ligand. The coordination of an alkyl pyridine ancillary moiety to the 2,6-bis(tetrazolyl)pyridine complex allowed us to enhance the solubility and thus the processability. The synthetic approach involved mild reaction conditions that involved a non-nucleophilic base and an adequate inorganic platinum(II) precursor. Moisture- and oxygen exclusion were not required, and the product was easily purified by repeated precipitation (Scheme 1). The emission intensity of the complex attained a

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Scheme 1. One-pot synthesis of platinum(II) complex **4** and a representation of the self-assembly process, going from luminescent aggregates to fibers and gels.

PLQY of up to 87% in thin films, with concentration-independent color and efficiency. We demonstrated its suitability as a dopant in solution-processed OLEDs. Furthermore, we discovered that this complex is also able to self-assemble into bright nanofibers, which can interlock to yield highly emissive gels (90% PLQY), thus constituting a versatile building block for luminescent supramolecular architectures.

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The one-pot synthetic procedure (Scheme 1) involves the dissolution of the tridentate ligand **1**[10] in acetonitrile heated to reflux and with the aid of diisopropylethylamine (DIPEA). The platinum(II) salt [PtCl$_2$(dmso)$_2$] (**2**)[11] was added together with the pyridine ligand **3**. The product (**4**) precipitated out of the reaction mixture as a yellow powder and was purified by recrystallization. Other platinum(II) salts, such as PtCl$_2$ or K$_2$[PtCl$_4$], did not yield the desired product, which might be attributed to their lower reactivity. In principle, any pyridine derivative could be employed, thus providing a versatile synthetic building block for solid-state luminescent architectures. However, ancillary ligands with shorter substituents afforded insoluble luminescent solids, thus impeding satisfactory purification. The absence or delayed addition of the pyridine derivative gave a non-luminescent brown-yellowish insoluble residue.

Complex **4** is non-emissive in dilute solution at room temperature. However, in a frozen CH$_2$Cl$_2$ matrix at 77 K and in thin films, it gives rise to a bright unstructured luminescence signal centered at 570 nm, and also shows an intense excitation band at around 450 nm, a feature that is not present in solution at room temperature (Figure 1). The PLQY and
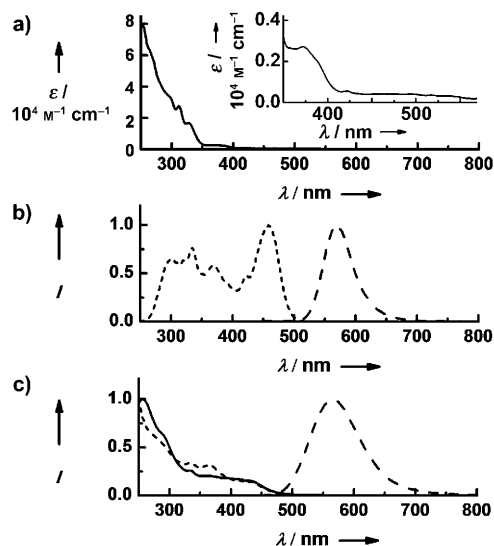

Figure 1. Spectroscopic properties of complex **4**. a) Absorption spectrum from a CH$_2$Cl$_2$ solution (10^{-5} M). Inset: Enlargement of the metal–ligand charge-transfer (MLCT) absorption band. b) Normalized excitation (••••, λ_{em} = 580) and emission spectra (-----, λ_{ex} = 420) in a frozen CH$_2$Cl$_2$ matrix (10^{-5} M). c) Normalized absorption (——), excitation (••••, λ_{em} = 580) and emission (-----, λ_{ex} = 420) spectra in PMMA matrices (10 wt%).

the emission spectra do not depend on the excitation wavelength. Compound **4** reaches up to 87% PLQY in neat films and poly(methyl methacrylate) (PMMA) matrices, and the emission and excitation spectra do not vary significantly with its concentration (Supporting Information, Figure S1). The PLQY and the radiative rate constants increase by more than 10% along with the concentration of **4**, while the nonradiative decay is reduced by a factor of almost two, which might correlate with the degree of organization of the aggregates,

reaching a maximum in the supramolecular gel (see below). Usually, however, platinum(II) complexes show rather low PLQYs and strongly concentration-dependent emission owing to aggregate or excimer formation. The photophysical characteristics of complex **4** point towards aggregation processes in the ground state that lead to excited triplet metal–metal–ligand charge-transfer (^{3}MMLCT) states, facilitated by the interaction between the axial d$_{z^2}$ orbitals of the central platinum(II) atoms. This effect only becomes evident in frozen matrices and in thin films where aggregate formation is favored, leading to the absorption and emission observed around 420 nm and 560 nm, respectively. The bright luminescence upon aggregation can be employed to monitor the assembling process with high sensitivity.

The luminescence of **4** in thin films makes it attractive for the use in electronic devices such as OLEDs. Iridium(III)-based emitters are quenched by triplet–triplet annihilation at doping levels as low as 5 wt%,[12] which is often too low for solution-processed devices.[13] Initially, we tested a simple device that employs a host matrix based on PVK (poly(N-vinyl carbazole)) and PBD (2-(4-biphenylyl)-5-(4-tert-butyl-phenyl)-1,3,4-oxadiazole; for details, see Supporting Information). The highest efficiency was reached with 10 wt% doping with **4**, and the maximum current efficiency $\eta_{c,max}$ was 15.6 cd A^{-1} (4.5 Lm W^{-1}) at a brightness of 203 cd m^{-2} (Supporting Information, Figure S2). The maximum brightness L_{max} was 11360 cd m^{-2}. We pursued an optimization of the charge transport properties (for details, see the Supporting Information) by blending the matrix with OXD-7 (1,3-bis(5-(4-tert-butylphenyl)-1,3,4-oxadiazol-2-yl)benzene).[14] Furthermore, QUPD (N,N'-bis(4-[6-[(3-ethyloxetane-3-yl)methoxy]-hexyloxy)phenyl]-N,N'-bis(4-methoxyphenyl)biphenyl-4,4'-diamine)[15] and OTPD (N,N'-bis(4-[6-[(3-ethyl-oxetane-3-yl)methoxy]-hexylphenyl]-N,N'-diphenyl-4,4'-diamine))[15] were employed in the optimized device. The maximum current efficiency was 13.2 cd A^{-1} (12.7 Lm W^{-1}) at a brightness of 1 cd m^{-2}. At 500 cd m^{-2}, the efficiency was 7.4 cd A^{-1} (5.7 Lm W^{-1}). The maximum brightness (L_{max}) was 2781 cd m^{-2} (Figure 2). Attempts to increase the concentration of **4** in the emissive layer yielded unsatisfactory device characteristics owing to inferior film-forming properties.

The PVK-based matrices are not good hosts for this class of complexes, for which aggregation plays a central role in the emission process. Indeed, we noticed a drop of the PLQY in doped PVK films relative to PMMA. Therefore, host polymers that do not affect the PLQY of the emitter while displaying better film-forming capacities at higher dopant concentrations are the object of ongoing research. Nonetheless, our devices perform quite well in comparison to sublimed platinum(II) complexes with N^C^N tridentate ligands ($\eta_{c,max}$ = 15–40 cd A^{-1}, L_{max} = 3500–12100 cd m^{-2})[16] or O^N^N^O Schiff base tetradentate units ($\eta_{c,max}$ = 1.6–31 cd A^{-1}, L_{max} = 3000–20000 cd m^{-2}).[17] The efficiency of small-molecule OLEDs is higher owing to a more sophisticated device configuration. However, solution-processable emitters would enable a cost-effective fabrication.

The soluble alkyl chains attached to the insoluble stacking chromophore render this complex a solution-processable gelator. Dissolving **4** in CHCl$_3$ and diffusing n-hexane into the
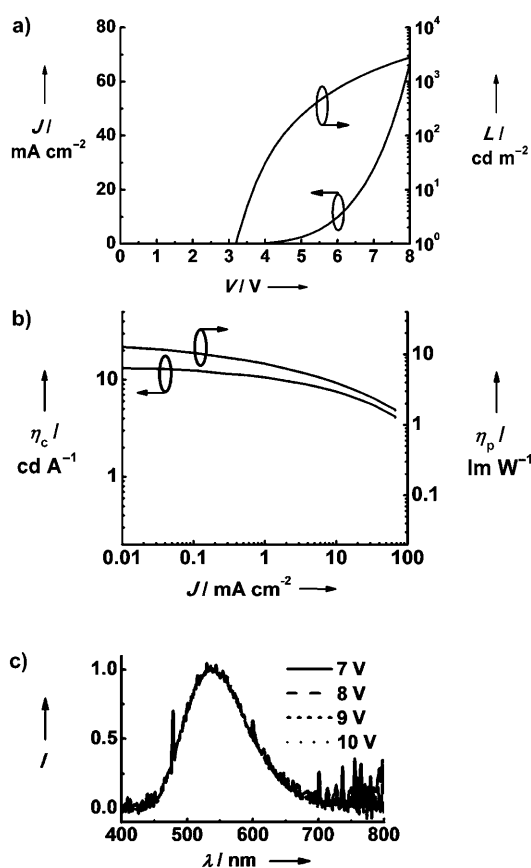
Figure 2. a) Current-density–voltage–luminance (*J–V–L*) curve and b) luminous efficiency η_c and power efficiency η_p versus current density of the optimized device. c) Electroluminescence spectra recorded at various applied voltages. Configuration: ITO/PEDOT:PSS/QUPD/OTPD/PVK:OXD-7:**4** (5 wt%)/TPBI/CsF/Al. ITO = indium tin oxide, PEDOT:PSS = poly(styrenesulfonate)-doped poly(3,4-ethylenedioxythiophene), TPBI = 1,3,5-tris(1-phenyl-1*H*-benzimidazol-2-yl)benzene.
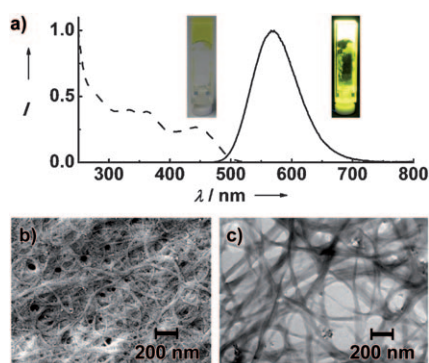

Figure 3. a) Emission (——, $\lambda_{ex}=420$) and excitation spectra (-----, $\lambda_{em}=580$) of the gel. Insets: Photographs of the luminescent gel. b) Top-view SEM image and c) TEM image of the gel.

Table 1: Photophysical data and device performance of complex **4**.

Sample	λ_{em} [nm][a]	PLQY [%][b]	τ [µs][a]	$k_r 10^{-4}$ [s^{-1}][c]	$k_{nr} 10^{-4}$ [s^{-1}][c]
CH$_2$Cl$_2$, 77 K	570	–	3.1	–	–
PMMA, 10 wt%[f]	566	76	0.84	91	28
PMMA, 25 wt%[f]	570	78	0.80	98	27
PMMA, 50 wt%[f]	567	74	0.78	94	34
PMMA, 75 wt%[f]	567	85	0.79	110	19
neat film	567	87	0.75	120	17
gel	569	90	0.72	125	14
fibers	572	84	0.64	131	25

OLEDs	V_{on}[d] [V]	L_{max} [cd m^{-2}]	$\eta_{c,max}$ [cd A^{-1}]	$\eta_{p,max}$ [lm W^{-1}]	CIE[e] [x,y]
PVK:PBD, 10 wt%[f]	6.4±1	11360±22	15.6	4.5	0.41, 0.51
PVK:OXD-7, 5 wt%[f]	3.1±1	2781±8	13.2	12.7	0.36, 0.53

[a] All of the data were measured by exciting at 420 nm (emission maxima) or 431 nm (lifetimes τ). [b] Average values for excitation wavelengths of 333, 365, and 420 nm. [c] k_r = radiative rate constant and k_{nr} = nonradiative rate constant were calculated according to the equations $k_r = \text{PLQY}/\tau$ and $k_{nr} = (1/\tau) - k_r$. [d] V_{on} = turn-on voltage. [e] CIE = Commission Internationale de l'Eclairage coordinates. [f] Loading with **4**.

colorless non-emissive solution affords a self-assembled yellow gel that appears highly luminescent under UV irradiation (Figure 3). A close inspection with SEM revealed a 3D network of fibers that are responsible for the structure of the emissive soft material, and TEM analysis showed the interlocking nature of the nanofibers (Figure 3). The spectroscopic features (Table 1, Figure 3) show that the gel is an efficient emitter with up to 90% PLQY. Self-assembly of platinum(II) complexes yielding luminescent liquid crystals[18] and aggregation-induced emission[19] have already been described. However, to the best of our knowledge, ours is the first platinum(II) complex capable of forming a solution-processable soft material with such elevated brightness. Moreover, as the complex does not emit in solution, the changes upon the formation of the assemblies are striking.

To further understand the structure of the assemblies, we isolated tangled and single nanofibers by direct addition of hexane to a CHCl$_3$ solution of **4**, which gives rise to a suspension of filaments. The SEM and TEM analysis (Figure 4 and Supporting Information, Figure S4) shows that the structures of about 80 nm diameter are constituted by fibrous subunits of about 20 nm cross-section, which points to a columnar array of aggregates. Spectrally resolved fluorescence microscopy (Figure 4) indicated that the emission of the single fibers coincides with the luminescence of the bulk assembly. The PLQY, spectra, and lifetimes of fibers deposited on a quartz slide (Table 1; Supporting Information, Figure S5) resemble those of the gel, showing that they can be considered as the supramolecular functional units of the soft material.

In conclusion, we developed a straightforward one-pot synthetic strategy affording a new class of platinum(II) triplet emitter with particular photophysical properties owing to aggregate formation. The self-assembly process can be monitored with high sensitivity by the turn-on of the emission
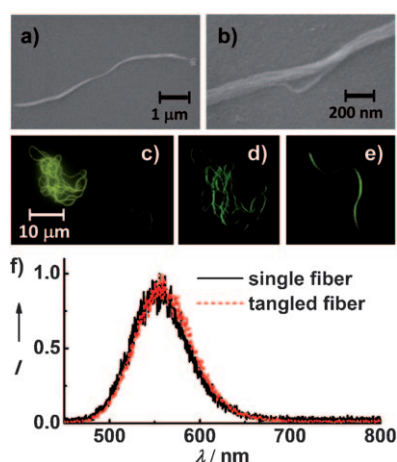
Figure 4. a, b) Top-view SEM images of a single nanofiber at different magnifications. c) Fluorescence microscopy image ($\lambda_{ex} = 360$–370 nm), and d, e) confocal microscopy images of nanofibers ($\lambda_{ex} = 440$ nm). f) Emission spectra of a single and of tangled nanofibers, $\lambda_{ex} = 440$ nm.

upon aggregation. The solution processability enables the formation of luminescent films and their use as dopants for OLEDs. Self-assembly of the monomers into bright supramolecular filaments can be induced; the filaments interlock and gelate to yield a highly emissive soft material.

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