Supramolecular Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713649759

4'-(9-Anthryl)-2,2':6',2''-terpyridine—a novel luminescent component for metallosupramolecular systems

Edwin C. Constable[a]; Diane R. Smith[a]
[a] Institut für Anorganische Chemie, Universität Basel, Basel, Switzerland

To cite this Article Constable, Edwin C. and Smith, Diane R.(1994) '4'-(9-Anthryl)-2,2':6',2''-terpyridine—a novel luminescent component for metallosupramolecular systems', Supramolecular Chemistry, 4: 1, 5 — 7
To link to this Article: DOI: 10.1080/10610279408029855
URL: http://dx.doi.org/10.1080/10610279408029855

SUPRAMOLECULAR CHEMISTRY, Vol. 4, pp. 5–7
Reprints available directly from the publisher
Photocopying permitted by license only

COMMUNICATION

4′-(9-Anthryl)-2,2′:6′,2″-terpyridine—a novel luminescent component for metallosupramolecular systems

EDWIN C. CONSTABLE* and DIANE R. SMITH

Institut für Anorganische Chemie, Universität Basel, Spitalstrasse 51, 4056 Basel, Switzerland

(Received January 7, 1994)

An anthryl-substituted 2,2′:6′,2″-terpyridine has been prepared, and the photochemical properties of the new ligand and its ruthenium and iron complexes studied.

INTRODUCTION

There is intense current interest in the design of photoaddressable supramolecular systems which might allow controlled and directional energy or electron transfer processes.[1] Recently, we have developed systematic synthetic routes to photoactive supramolecular polymers of defined nuclearity based upon the use of kinetically inert d^6 metal centres (ruthenium(II), cobalt(III) and osmium(II)).[2] In these studies we have concentrated upon the introduction of metal-centred photoactive domains and have adopted linear and dendritic methodologies. In this paper we describe an extention of this methodology in which a pendant photoactive anthracene group is attached to a metal-binding domain. Anthracenes are luminescent and photoexcitation yields a singlet state which undergoes an inter-system-crossing to generate a triplet state which decays in a radiative manner to the ground (singlet) state. Anthracene substituents may act as photoaddressable probes or as primary photocentres in supramolecular systems.[3]

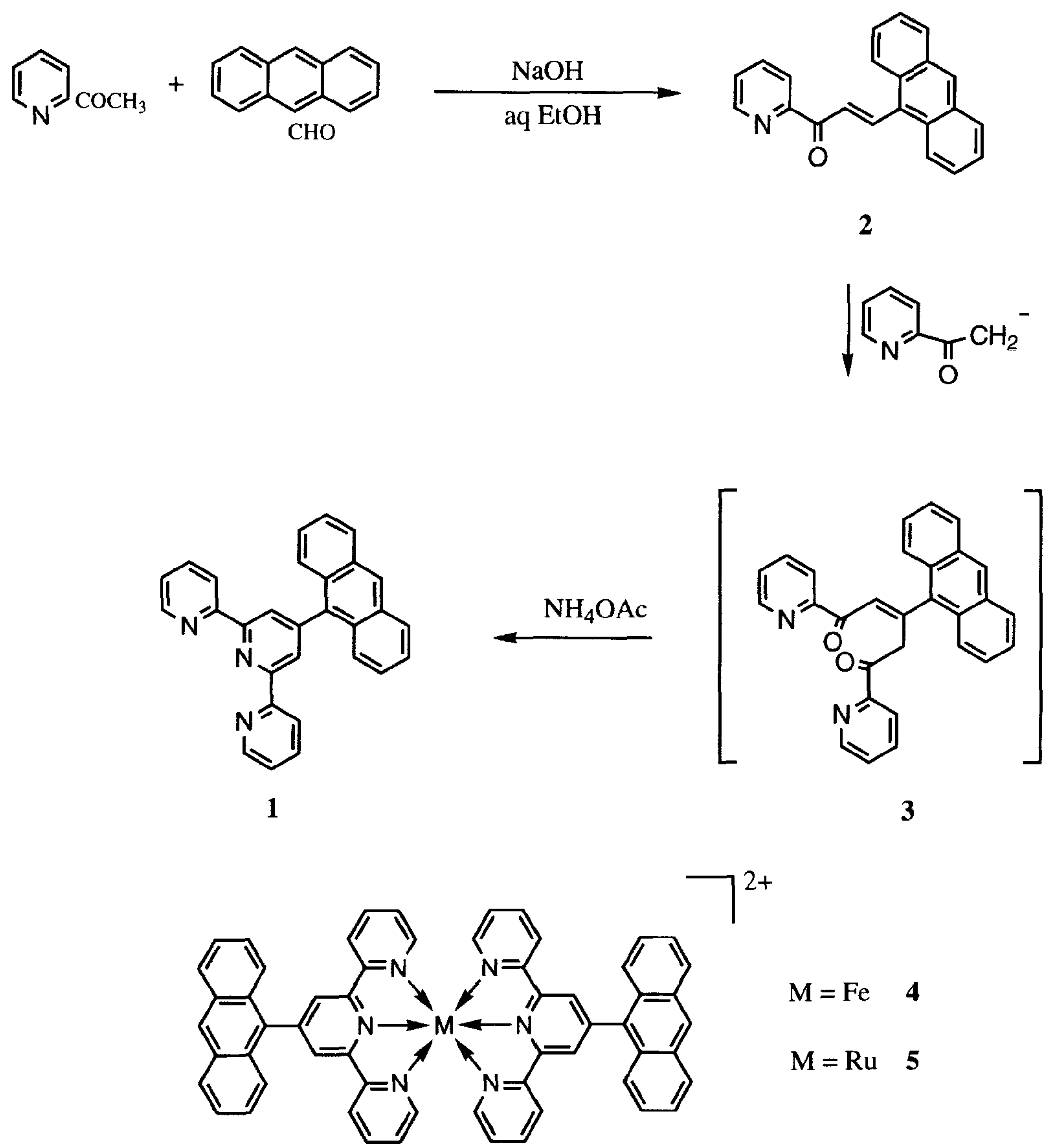
For the first generation of these complexes we have prepared the new ligand Antpy, **1**. This ligand was designed because it might allow efficient and specific energy transfer between anthracene-based excited states and the metal-manifold in its transition metal complexes. Although the reaction of arylaldehydes with an excess of 2-acetylpyridine in the presence of base often yields 1,5-bis(2-pyridyl)-4-aryl-1,5-pentanediones,[4] the reaction of 9-anthraldehyde with 2-acetylpyridine under a variety of conditions only yielded the enone **2**.[5] This is in marked contrast to the behaviour of the chalcone obtained from the reaction of 2-acetylpyridine with benzaldehyde, which is extremely reactive with nucleophiles. Attempts to convert **2** to **1** by reaction with an excess of 2-acetylpyridine or with the Kröhnke reagent 2-oxo-2-(2-pyridyl)ethylpyridinium iodide[6] in the presence of $[NH_4][OAc]$ were unsuccessful and only unreacted **2** was recovered. Accordingly, we have developed a method for the conversion of the enone to the 1,5-dicarbonyl **3** using more rigorous conditions than those usually adopted. The reaction of **2** with the enolate of 2-acetylpyridine, generated *in situ* from the reaction of 2-acetylpyridine with ^{t}BuOK in thf, yielded **3** which was not isolated, but was cyclised directly by reaction with $[NH_4][OAc]$ in aerobic conditions to yield **1** in 63% yield.[7]

Both compounds **1** and **2** are luminescent. Compound **1** is intensely luminescent (emission maximum 425 nm, Fig 1a), and the bonding of the anthryl group to the 2,2′:6′,2″-terpyridinyl moiety does not appear to affect the photophysical properties of the anthracene group. In addition, the absorption spectra of solutions of the compound are typical of fluorescent substances and do not obey Beer's Law.

The iron(II) complex of **1**, $[Fe(\mathbf{1})_2][PF_6]_2$ (**4**),[8] is readily formed by the reaction of **1** with iron(II) salts followed by precipitation of the hexafluorophosphate salt. The electronic spectrum exhibits a ligand-centred absorption band at 253 nm and an iron centred absorption band at 565 nm. However, the complex **4** was non-luminescent, with the iron quenching the luminescence of the anthracene. No luminescence was

---

* To whom correspondence should be addressed.



observed when solutions of **4** were excited at 253 nm or 565 nm.

In contrast to this behaviour, however, the ruthenium(II) complex, $[Ru(\mathbf{1})_2][PF_6]_2$ **5**,[8] is luminescent. We have completed a preliminary comparative study of the photochemical properties of the complex and the free ligand at room temperature using acetonitrile solutions which contained equal concentrations (1.0×10^{-5} mol) of anthracene groups.

The electronic absorption spectrum of the ruthenium complex showed a ligand-based absorption band with a λ_{max} at 253 nm, i.e. the same as for the free ligand, and a comparatively weak MLCT absorption band at 485 nm.

Excitation of the complex at 253 nm produced an emission spectrum almost identical to that of the free ligand (Fig 1a), with the emission essentially entirely from the ligand and with little evidence for any metal-centred emission.

Excitation of the complex at the MLCT band (485 nm, Fig 1b), resulted in a very weak emission from the anthracene group; this suggests that there is little, if any, long range energy transfer from the metal to the anthracene group. In addition, the observation of a very weak emission band at 650 nm is indicative of a ruthenium-centred emission. The absence of energy transfer processes in the complex suggests that there is little, or no, interaction between the two photoactive centres in their excited states. Furthermore the observation of only ligand emission on excitation at 253 nm and only a metal-centred emission on excitation at 485 nm indicates that the two photoactive centres

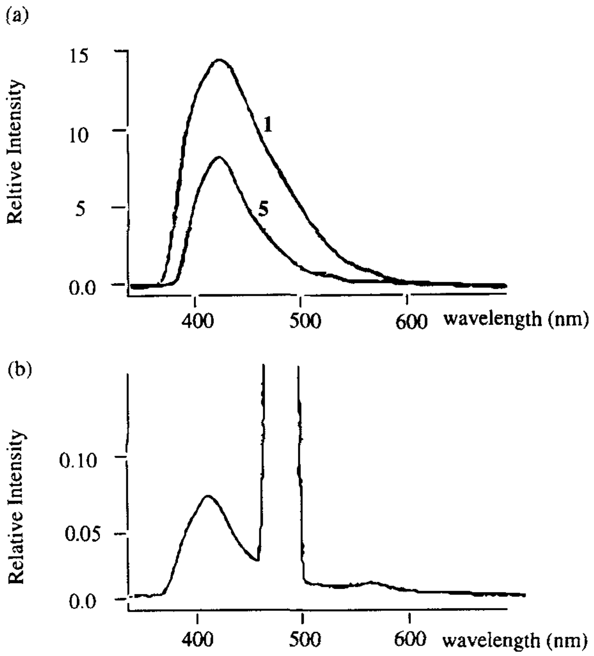


Figure 1 Emission spectra of acetonitrile solutions of (a) the ligand 1 (1.0×10^{-5} M) and ruthenium complex **5** (0.5×10^{-5} M) on excitation at 253 nm and (b) the ruthenium complex **5** (0.5×10^{-5} M) on excitation at 485 nm.

are functioning independently from each other. This is currently undergoing further investigation.

ACKNOWLEDGEMENTS

We gratefully acknowledge the SERC for a post doctoral Fellowship to DRS and the Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forschung (Grant number: 21-37325.93) for financial support.

NOTES AND REFERENCES

1 See for example, Denti, G.; Serroni, S.; Sampagna, S.; Juris, A.; Ciano, M.; Balzani, V.; in *Perspectives in Coordination Chemistry* (Williams, A.F., Floriani, C. and Mernach, A.E., eds.), VHCA, Basel, **1992**.

2 Constable, E.C.; Cargill Thompson, A.M.W.; Greulich, S.; *J. Chem. Soc., Chem. Commun.* **1993**, 3027. Newkome, G.R.; Cardullo, F.; Constable, E.C.; Moorefield, C.N.; Cargill Thompson, A.M.W.; *J. Chem. Soc., Chem. Commun.* **1993**, 925. Barigelletti, F.; Flamigni, L.; Balzani, V.; Collin, J.-P.; Sauvage, J.-P.; Sour, A.; Constable, E.C.; Cargill Thompson, A.M.W.; *J. Chem. Soc., Chem. Commun.* **1993**, 942. Constable, E.C.; Cargill Thompson, A.M.W.; *J. Chem. Soc., Dalton Trans.* **1992**, 3467.

3 Murru, M.; Parker, D.; Williams, G.; Beeby, A.; *J. Chem. Soc., Chem. Commun.* **1993**, 1116. de Silva, A.P.; Sandanayake, K.R.A.S.; *J. Chem. Soc., Chem. Commun.* **1989**, 1183. Konopelski, J.P.; Kotzyba-Hilbert, F.; Lehn, J.-M.; Desvergne, J.-P.; Fagès, F.; Castellan, A.; Bouas-Laurent, H.; *J. Chem. Soc., Chem. Commun.* **1985**, 433.

4 Constable, E.C.; Ward, M.D.; *J. Chem. Soc., Dalton Trans.* **1989**, 1405. Potts, K.T.; Cipullo, M.J.; Ralli, P.; Theodoridis, G.; *J. Org. Chem.* **1982**, *47*, 3027. Constable, E.C.; Cargill Thompson, A.M.W.; Tocher, D.A.; *Supramol. Chem.* **1993**, *3*, 9. Constable, E.C.; Lewis, J.; Liptrot, M.C.; Raithby, P.R.; *Inorg. Chim. Acta* **1990**, *178*, 47.

5 **2**: Aqueous NaOH (10 mL of a 1.5 M solution) was added to a stirred solution of 2-acetylpyridine (1.20 g, 10 mmol) and 9-anthraldehyde (2.06 g, 10 mmol) in ethanol (20 mL). After stirring for 4 hours at r.t., the orange precipitate was isolated by filtration, recrystallisation from MeOH afforded **2** as orange needles (2.86 g, 93%). [EIMS: *m/z* 309 $(M)^+$; IR: 1670 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 7.50$ (m, 4H), 7.92 (td, 2H), 8.03 (m, 2H), 8.29 (AB, $J = 16$ Hz, 1H and s, 1H), 8.37 (m, 2H), 8.48 (s, 1H), 8.70 (d, 1H), 8.94 (AB, $J = 16$ Hz, 1H)].

6 Kröhnke, F.; *Synthesis* **1976**, 1.

7 **1**: 2-Acetylpyridine ; 0.1 mL, 0.84 mmol) was added to a stirred solution of ^{t}BuOK (0.14 g, 1.3 mmol) in anhydrous thf (20 mL). After stirring at r.t. in an inert atmosphere for 2 h, **2** (0.20 g, 0.64 mmol) was added to the now yellow reaction mixture. The solution was stirred at r.t. for 14 hours during which time a dark red colour developed. NH_4OAc (1 g) and EtOH (20 ml) were added sequentially and the mixture heated at reflux for 4 hours. Removal of the solvent *in vacuo* afforded a brown gum from which the ligand was precipitated out by the addition of water. Recrystallisation from $CHCl_3$/MeOH afforded **1** as pale yellow needles (68 mg, 63%). [EIMS: *m/z* 409 $(M)^+$; ^1H NMR ($CDCl_3$): $\delta = 7.35$ (m, 4H), 7.46 (t, 2H), 7.71 (d, 2H), 7.92 (t, 2H), 8.07 (d, 2H), 8.54 (s, 2H), 8.63 (m, 4H), 8.80 (d, 2H)].

7 **4**: $[Fe(H_2O)_6][SO_4]$ (12 mg, 0.046 mmol) and **1** (40 mg, 0.098 mmol) were stirred in MeOH (5 ml) at r.t. and after dissolution was complete, methanolic NH_4PF_6 was added. The dark red needles of **4** that precipitated were isolated by filtration (48 mg, 90%).

5: $RuCl_3$ (13 mg, 0.061 mmol) and **1** (25 mg, 0.061 mmol) were heated at reflux in MeOH for 1 h. The brown solid $[Ru(\mathbf{1})Cl_3]$ was isolated by filtration and this then added to a further aliquot of **1** (25 mg, 0.061 mmol) in EtOH. This mixture was heated at reflux for 2 h and after cooling **5** was precipitated from solution by the addition of methanolic NH_4PF_6 as an orange-brown solid (65 mg, 88%). Laser desorption TOFMS: *m/z* 1065 $([Ru(\mathbf{I})_2][PF_6])^+$: 920 $([Ru(\mathbf{I})_2])^+$.