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Luminescent properties of carbon-rich starburst gold(I) acetylide complexes. Crystal structure of [TEE][Au(PCy$_3$)]$_4$ ([TEE]H$_4$ = tetraethynylethene)

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Abstract

Two carbon-rich starburst gold(I) acetylide complexes [TEE][Au(PCy$_3$)]$_4$ (**3**, [TEE]H$_4$ = tetraethynylethene) and [TEB][Au(PCy$_3$)]$_3$ (**6**, [TEB]H$_3$ = 1,3,5-triethynylbenzene) were prepared and their UV–vis absorption, emission and excitation spectra have been recorded. In fluid CH$_2$Cl$_2$ solutions, **3** exhibits prompt $^1(\pi\pi^*)$ fluorescence with λ_{0-0} and $\lambda_{\max}$ at 413 and 428 nm, respectively, while **6** displays $^3(\pi\pi^*)$ phosphorescence with λ_{0-0} and $\lambda_{\max}$ at 446 and 479 nm, respectively. The crystal structure of **3**·CH$_2$Cl$_2$ has been determined.

Keywords: Acetylide; Gold; Cross-conjugation; Phosphorescence; Fluorescence

1. Introduction

The strong affinity of carbon-coordinating ligands towards gold ion is manifested by the poor recovery of gold from carbonaceous gold ores [1], and accounts for the rich chemistry reported for organogold compounds [2]. Among the organogold complexes known in the literature, gold(I) acetylides have received considerable attention owing to their stability, easy preparation, novel solid-state structures [3], and interesting spectroscopic properties, such as non-linear optical response [4] and photoluminescence [5]. One of our objectives is to investigate the potential applications of luminescent carbon-rich gold(I) acetylide complexes as optoelectronic materials.

Our methodology involves attachment of the [Au(PCy$_3$)]$^+$ (PCy$_3$ = tricyclohexylphosphane) moiety, through Au–C≡C ligation, onto conjugated carbon-rich organic substrates containing peripheral oligoethynyl group(s) in order to 'switch on' or modify its photoluminescent properties. [Au(PCy$_3$)]$^+$ is isolobal to H$^+$ [6], and the former has recently been shown to induce phosphorescence in unsaturated carbon-rich compounds through effcient spin–orbit coupling [7]. Compared to Pt(II), the d^{10} closed-shell configuration of Au(I) does not allow low-lying d–d excited state(s), and hence the lifetime and emission quantum yield of intraligand triplet excited states would not be affected by internal quenching mechanisms. Tricyclohexyl phosphane, compared to triarylphosphane and other trialkylphosphane with small cone angles, is a judicious ancillary group for spectroscopic studies because it has no low-lying ligand-localized excited states and its bulkiness (cone angle 170°) disfavors π–π and Au–Au interactions, which could affect emission properties through formation of ππ* excimers, $^3(d\sigma^*p\sigma)$ excited states, or substrate-binding exciplexes as reported for polynuclear Au(I) compounds [8].

In 1992, Schmidbaur [9] reported the synthesis of [C][Au(PCy$_3$)]$_4$ (**1**) (Chart 1) which could be regarded as the lowest homologue in the series [C$_x$][Au(PCy$_3$)]$_y$. Subsequently, we [7] reported the structure and spectroscopic properties of Cy$_3$PAu(C≡C)$_n$AuPCy$_3$ (**2**, n = 1–4) and found that the acetylenic $^3(\pi\pi^*)$ transitions acquire sufficient allowedness via Au spin–orbit cou-

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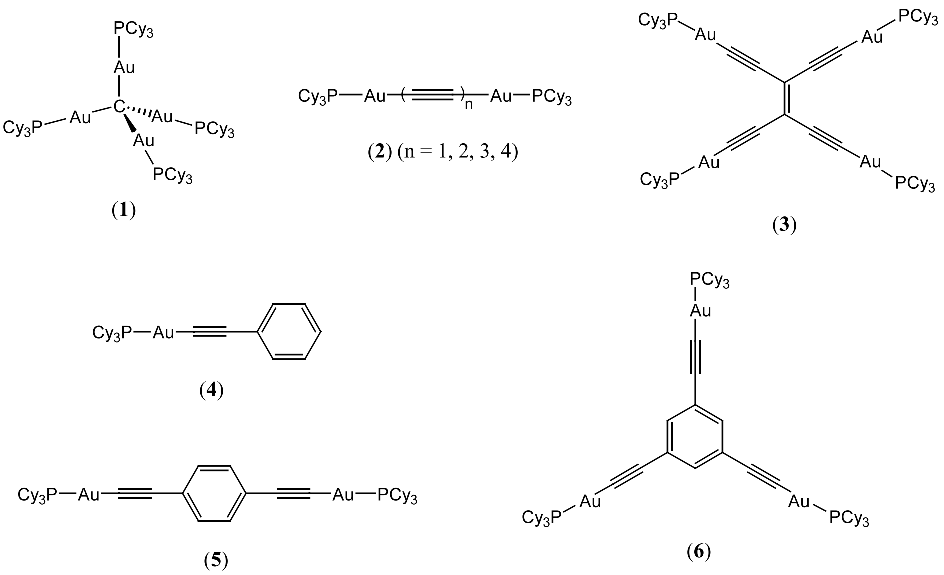

Chart 1.

pling to appear prominently in both the electronic absorption and emission spectra. The energy for the 0–0 transitions of $[C_{2n}][Au(PCy_3)]_y$ decreases with the increment of the acetylenic conjugation length (that is, the n value) and the limiting λ_{0-0} value ($n = 8$) for the acetylenic $^3(\pi\pi^*)$ emission is estimated to be 910 nm [7b]. Herein we report complex $[TEE][Au(PCy_3)]_4$ (**3**, $[TEE]H_4$ = tetraethynylethene) which is a higher homologue of the series $[C_x][Au(PCy_3)]_y$, where $x = 10$, $y = 4$. Significantly, this complex possesses a cross-conjugated [10] component that is different from the linear fully conjugated gold(I) oligoynes **2**.

Also reported in the present work is the spectroscopic properties of complex $[TEB][Au(PCy_3)]_3$ (**6**, $[TEB]H_3$ = 1,3,5-triethynylbenzene), which represents the trinuclear analogue of mononuclear $[ethynylbenzene][Au(PCy_3)]$ (**4**) and dinuclear $[DEB][Au(PCy_3)]_2$ (**5**, $[DEB]H_2$ = 1,4-diethynylbenzene) complexes [11]. Both **3** and **6** have starburst-like cross-conjugated skeletons, which are potential modules for extended assemblies such as hyper-branched polymers and dendrimers. The crystal structure and NLO property of the analogous complex $[TEB][Au(PPh_3)]_3$ has been reported [12]. The trinuclear Pt(II) and Pd(II) 1,3,5-triethynylbenzene complexes were previously reported to be useful building blocks for metallodendrimers [13].

2. Experimental

2.1. Materials and general procedure

All starting materials were used as received. The compounds $[(Cy_3P)AuCl]$ [7a] and tetrakis(trimethylsilyl)tetraethynylethene ($[TEE](SiMe_3)_4$) [14] were prepared according to literature methods. Elemental analyses were performed by the Institute of Chemistry at Chinese Academy of Sciences, Beijing. Fast atom bombardment (FAB) mass spectra were obtained on a Finnigan Mat 95 mass spectrometer. Nuclear magnetic resonance spectra were recorded on Avance400 Bruker FT-NMR spectrometers. UV–vis spectra were recorded on a Perkin–Elmer Lambda 19 UV–vis spectrophotometer. Emission spectra were obtained on a SPEX Fluorolog-2 model F111 fluorescence spectrophotometer. Emission lifetime measurements were performed with a Quanta Ray DCR-3 pulsed Nd:YAG laser system (pulse output 355 or 266 nm, 8 ns). Errors for λ values (± 1 nm) and τ ($\pm 10\%$) are estimated.

2.2. Syntheses

2.2.1. $[TEE][Au(PCy_3)]_4$ (**3**)

Solid sodium hydroxide (0.03 g) was added to a mixture of $[(Cy_3P)AuCl]$ (0.21 g, 0.4 mmol) and $[TEE](SiMe_3)_4$ (0.04 g, 0.1 mmol) in methanol (20 ml). The suspension was stirred for 12 h and the precipitate was collected and washed with deionized water, methanol, and diethyl ether. Recrystallization from dichloromethane/diethyl ether gave yellow plates. Yield: 0.05 g, 25%. Anal. Calc. for $C_{82}H_{132}P_4Au_4 \cdot CH_2Cl_2$: C, 47.14; H, 6.39; Found: C, 47.23; H, 6.19%. FABMS: m/z 2030 $[M^+]$, 1750 $[M^+ - PCy_3]$, 1554 $[M^+ - AuPCy_3]$. ^1H-NMR ($CDCl_3$): $\delta = 1.94$–1.18 (m, Cy). $^{13}C\{1H\}$-NMR ($CDCl_3$): $\delta = 145.4$ (d, $^2J_{PC} = 135$ Hz, Au–C≡C), 115.6 (s, C=C), 103.7 (d, $^3J_{PC} = 25.0$ Hz, Au–C≡C), 33.3 (d, $^1J_{PC} = 27.2$ Hz, Cy), 30.5 (s, Cy), 27.2 (d, $^2J_{PC} = 11.5$ Hz, Cy), 26.0 (s, Cy). $^{31}P\{1H\}$-NMR ($CDCl_3$): $\delta = 56.1$.

2.2.2. *[TEB][Au(PCy₃)]₃* (**6**)

Sodium methoxide (0.04 g) was added to a mixture of $[(Cy_3P)AuCl]$ (0.21 g, 0.4 mmol) and 1,3,5-triethynylbenzene (0.015 g, 0.1 mmol) in dichloromethane/methanol (1/1, 20 ml). The solution was stirred for 12 h and evaporated to dryness under reduced pressure. The residue was collected and washed with deionized water, methanol and diethyl ether. Recrystallization from dichloromethane/diethyl ether gave colorless needles. Yield: 0.03 g, 20%. Anal. Calc. for $C_{66}H_{102}P_3Au_3$: C, 50.19; H, 6.51; Found: C, 50.12; H, 6.90%. FABMS: m/z 1580 [M^+], 1300 [$M^+ - PCy_3$], 1104 [$M^+ - AuPCy_3$]. ^{1}H-NMR ($CDCl_3$): $\delta = 7.45$ (s, 3H, Ph*H*), 2.00–1.25 (m, 33H, Cy). ^{13}C{1H}-NMR ($CDCl_3$): $\delta = 137.4$ (d, $^2J_{PC} = 132$ Hz, Au–*C*≡C), 136.4 (s, Ph), 126.2 (s, Ph), 104.9 (d, $^3J_{PC} = 24.4$ Hz, Au–C≡*C*), 34.8 (d, $^1J_{PC} = 27.7$ Hz, Cy), 32.2 (s, Cy), 28.8 (d, $^2J_{PC} = 11.7$ Hz, Cy), 27.6 (s, Cy). ^{31}P{1H}-NMR ($CDCl_3$): $\delta = 56.5$.

2.3. *X-ray crystallography*

Pale yellow crystals of $[TEE][Au(PCy_3)]_4 \cdot CH_2Cl_2$ (**3**·CH_2Cl_2) were obtained by vapor diffusion of diethyl ether into a dichloromethane solution. Crystal data: $C_{83}H_{134}Au_4Cl_2P_4$, $M = 2114.55$, crystal size $= 0.40 \times 0.25 \times 0.20$ mm^3, monoclinic, $P2_1/c$, $a = 24.590(5)$, $b = 22.577(5)$, $c = 17.751(4)$ Å, $V = 9853(4)$ Å^3, $Z = 4$, $D_{calc} = 1.426$ g cm^{-3}, $\mu = 6.091$ mm^{-1}, $F(000) = 4168$, $T = 253$ K. A total of 14603 independent reflections were collected on a MAR diffractometer (λ(Mo–K$_\alpha$) = 0.71073 Å). The structure was solved by direct method employing SIR-97 program and refined by full-matrix least-squares treatment on F^2 using SHELXL-97 program. The positions of H atoms were calculated based on riding mode with thermal parameters equal to 1.2 times that of the associated C atoms and participated in the calculation of final R-indices: $R = 0.054$, $wR = 0.16$, GoF = 1.005 for 14603 reflections with $I > 4\sigma(I)$ and 467 variable parameters (residual $\rho = +1.64, -1.23$ e Å^{-3}).

3. Results and discussion

3.1. *Synthesis and characterization of carbon-rich starburst Au(I) acetylide complexes*

The carbon-rich starburst Au(I) acetylide complexes **3** and **6** were prepared as air-stable solid by reaction of $[TEE](SiMe_3)_4$ and $[TEB]H_4$ with $[(Cy_3P)AuCl]$, respectively, in methanolic solution in the presence of a strong base. The ^{31}P{1H}-NMR spectra of **3** and **6** show a singlet signal at 56.1 and 56.5 ppm, respectively, suggesting that the phosphane ligands in each compound are chemically equivalent. The acetylenic units are readily identified in the ^{13}C{1H}-NMR spectra, since the α-acetylenic carbon coordinated to the Au atom appears as a doublet signal at ~140 ppm with $^2J_{PC}$ being ~130 Hz, and the β-acetylenic carbon is observed as a doublet at ~105 ppm with $^3J_{PC}$ being ~25 Hz, both of which are in agreement with related values for complexes **2** [7], **4** and **5** [11]. The ethene carbon singlet shifts downfield from 80.1 ppm for tetraethynylethene and 101.0 ppm for $[TEE](SiMe_3)_4$ [14] to 115.6 ppm for **3**, and this is due to charge transfer from the TEE ligand to the Au(I).

Complex **3** constitutes the first per-metalated derivative of tetraethynylethene. The molecular structure of **3**·CH_2Cl_2 has been determined by X-ray crystallography at −25 °C and is shown in Fig. 1; selected bond lengths and angles are listed in Table 1. Similar with the reported crystal structures of organic and $Pt(PR_3)_2$-bound derivatives of tetraethynylethene [15], the ligation of $[Au(PCy_3)]^+$ to tetraethynylethene results in a distorted structure, as revealed by the side view of **1** shown in Fig. 1 (bottom). In this structure, all the bond angles with acetylenic carbon and gold atoms as vertexes (171(1)–179.1(4)°) slightly deviate from linearity. The torsion angles P1–C3–C4–P2 (4.1°) and P3–C3–C4–P4 (12.2°) demonstrate significant deviation of the Au(I)-ligated tetraethynylethene framework from planarity, presumably due to crystal packing effects.

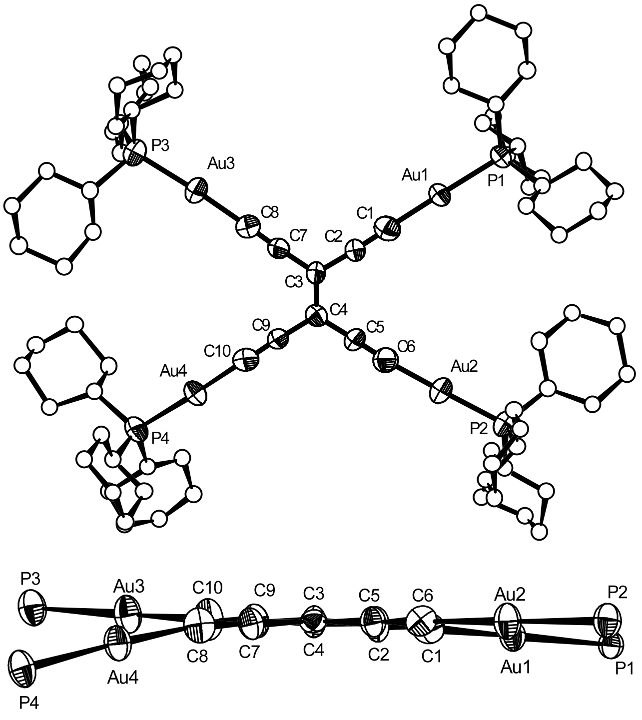

Fig. 1. Perspective (top) and side (bottom, Cy groups omitted for clarity) view of the molecular structure in **3**·CH_2Cl_2.

Table 1
Selected bond lengths (Å) and bond angles (°) of **3**·CH_2Cl_2

Bond lengths			
Au1–C1	1.98(1)	Au1–P1	2.300(3)
Au2–C6	2.01(1)	Au2–P2	2.293(4)
Au3–C8	2.02(2)	Au3–P3	2.298(4)
Au4–C10	1.98(1)	Au4–P4	2.291(3)
C1–C2	1.24(2)	C2–C3	1.45(2)
C3–C4	1.37(2)	C3–C7	1.43(2)
C4–C9	1.44(2)	C4–C5	1.44(2)
C5–C6	1.18(2)	C7–C8	1.19(2)
C9–C10	1.22(2)		
Bond angles			
C1–Au1–P1	179.1(4)	C6–Au2–P2	178.3(4)
C8–Au3–P3	176.7(4)	C10–Au4–P4	176.4(4)
C2–C1–Au1	179(1)	C1–C2–C3	176(2)
C4–C3–C7	124(1)	C4–C3–C2	119(1)
C7–C3–C2	117(1)	C3–C4–C9	120(1)
C3–C4–C5	123(1)	C9–C4–C5	117(1)
C6–C5–C4	178(2)	C5–C6–Au2	175(1)
C8–C7–C3	178(1)	C7–C8–Au3	178(2)
C10–C9–C4	178(1)	C9–C10–Au4	171(1)

3.2. Absorption and emission spectra

The absorption and emission data for **3** and **6** are listed in Table 2. As depicted in Fig. 2, the intriguing spectral feature in the absorption spectrum of **3** is the finely structured S_0–S_1 transition with a sharp λ_{0-0} line at 396 nm, which is red-shifted from the λ_{0-0} of ~330 nm for tetraethynylethene and 354 nm for [TEE]$(SiMe_3)_4$ [14]. Orbital interaction between tetraethynylethene and the Au 5d orbitals is invoked to account for the red-shift in transition energy [7]. Additionally, the slightly structured band with λ_{max} at 285 nm is assigned to the S_0–S_2 transition. Upon excitation at 350 nm, a CH_2Cl_2 solution of **3** emits intense blue light with λ_{0-0} and λ_{max} at 413 and 428 nm respectively. The short lifetime (< 0.05 μs) and small Stokes shift (from 396 to 413 nm, 1040 cm^{-1}) indicate that this emission is S_1–S_0 prompt fluorescence.

The mirror-symmetrical relationship between the emission and excitation spectra of **3** in glassy 2-methyltetrahydrofuran solution at 77 K is depicted in Fig. 3. At $\sim 1 \times 10^{-5}$ M, a well-structured emission in the range of 404–550 nm with dual vibronic progressions of 1970 and 1390 cm^{-1} is observed. The perfect overlap of the λ_{0-0} bands at 404 nm between the emission and excitation spectra together with the short lifetime (< 0.05 μs) signify the nature of this emission as $^1(\pi\pi^*)$(TEE), in line with the fluid solution. This finding is different from previous studies on oligoyne [7] and oligo(phenylethynyl) [11] Au(I) complexes that exhibit long-lived T_1–S_0 phosphorescence and/or S_1–S_0 delayed fluorescence through triplet-triplet annihilation. The reason for the lack of observable long-lived emission for **3** could be that the T_1 excited state of **3** occurs at a very low energy, which may lead to very low quantum yield for the $T_1 \rightarrow S_0$ phosphorescence. We suggest that the cross-conjugated structure may give rise to a low-energy T_1 excited state, although its contribution to the stabilization of the S_1 excited state is expected to be small [16]. Further clarification of this proposal requires more experimental and theoretical endeavors.

For **6** (Fig. 4), the λ_{0-0} for $S_0 \rightarrow S_1$ transition recorded in CH_2Cl_2 solution at 298 K appears at 285 nm, which is comparable to that of 281 nm for **4** but noticeably blue-shifted from that of 323 nm for **5** [11]. This is nevertheless reasonable, because the conjugation length for **6** is the same as that for **4** but shorter than that for **5**, where the two ethynyl group are located at the para positions of the benzene ring. The emission spectrum of **6** exhibits vibronic structure with dual progressions of 2055 and 1545 cm^{-1}. The corresponding emission lifetime of 285 μs is substantially longer than those for for **4** and **5** (18–81 μs), indicating $^3(\pi\pi^*)$(TEB) excited-state nature for this emission. The λ_{0-0} energy (446 nm) for this phosphorescence is higher than that of 488 nm for **5**, in agreement with the absorption data, but lower than that of 419 nm for **4**. We infer that the cross-

Table 2
Absorption and emission data of [TEE]$(SiMe_3)_4$, **3** and **6**

	Absorption [a] λ_{max}/nm ($\varepsilon / \times 10^4$ dm^3 mol^{-1} cm^{-1})	Emission λ_{max}/nm (τ/μs; ϕ [b])
[TEE][Au(PCy_3)]$_4$ (**3**)	229 (3.56), 240 (5.71), 252 (1.52), 278 (sh, 2.31), 287 (3.72), 299 (sh, 1.37), 350 (1.65), 367 (3.10), 376 (4.04), 396 (6.43)	(CH_2Cl_2, 298 K) 413, 428 (< 0.05 [c]; 0.22), 448 (sh) (MeTHF glass, 77 K) [d] 404 (< 0.05) [c], 428, 439, 457, 470 (solid, 298 K) 448 (< 0.05) [c] (solid, 77 K) 461 (< 0.05) [c]
[TEE]$(SiMe_3)_4$	229 (0.97), 260 (sh, 0.66), 271 (0.93), 287 (0.83), 317(sh,1.39), 330 (2.37), 339 (3.00), 354 (3.76)	(CH_2Cl_2, 298 K) 348, 372 (sh), 381 (< 0.05 [c]; 0.10), 398 (sh)
[TEB][Au(PCy_3)]$_3$ (**6**)	235 (3.67), 261 (sh, 3.94), 272 (6.31), 285 (6.83), 324 (0.23), 334 (0.19)	(CH_2Cl_2, 298 K) 446, 479 (285; 0.46), 448 (sh) (MeTHF glass, 77 K) [d] 443 (sh), 454 (975), 473, 488 (solid, 298 K) 454 (945), 480, 491 (sh) (solid, 77 K) 452 (1053), 471, 501

[a] In CH_2Cl_2 solution at 298 K.
[b] Quinine sulfate in degassed 0.1 N sulfuric acid as reference ($\phi_r = 0.546$).
[c] Short lifetime cannot be measured accurately due to instrumental limits.
[d] In glassy 2-methyltetrahydrofuran solution at 77 K.

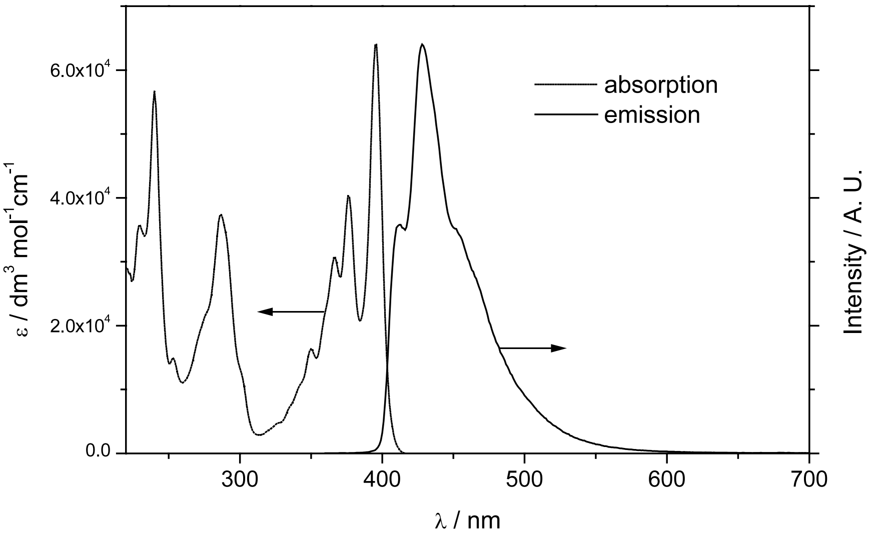

Fig. 2. Absorption and emission ($\lambda_{ex} = 350$ nm) spectra of **3** in CH_2Cl_2 solution (8.9×10^{-6} mol dm^{-3}) at 298 K.

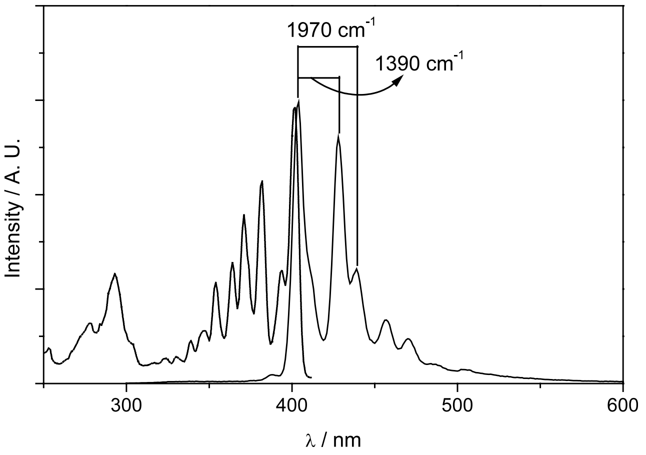

Fig. 3. Normalized emission ($\lambda_{ex} = 350$ nm, solid line) and excitation ($\lambda_{em} = 428$ nm, dotted line) spectra of **3** in glassy 2-methyltetrahydrofuran solution ($\sim 1 \times 10^{-5}$ mol dm^{-3}).

conjugation between the three [C≡C–Au(PCy_3)] moieties in complex **6** plays a key role in stabilizing the triplet $^3(\pi\pi^*)$(TEB) excited state. Interestingly, we note that this emission energy is identical to that for [TEB][Pd(PEt_3)$_2$Cl]$_3$ in alcoholic glass at 77 K (446 nm) [13c], confirming the intraligand $^3(\pi\pi^*)$(TEB) nature for this emission.

4. Concluding remarks

The carbon-rich starbust multinuclear Au(I) acetylide complexes synthesized and investigated in the present study has allowed correlation of emission properties with molecular structure for the [C_x][Au(PCy_3)]$_y$ series of compounds. The spectroscopic nature of these Au(I) complexes are affected to varying degrees by the respective carbon-rich conjugated/cross-conjugated or-

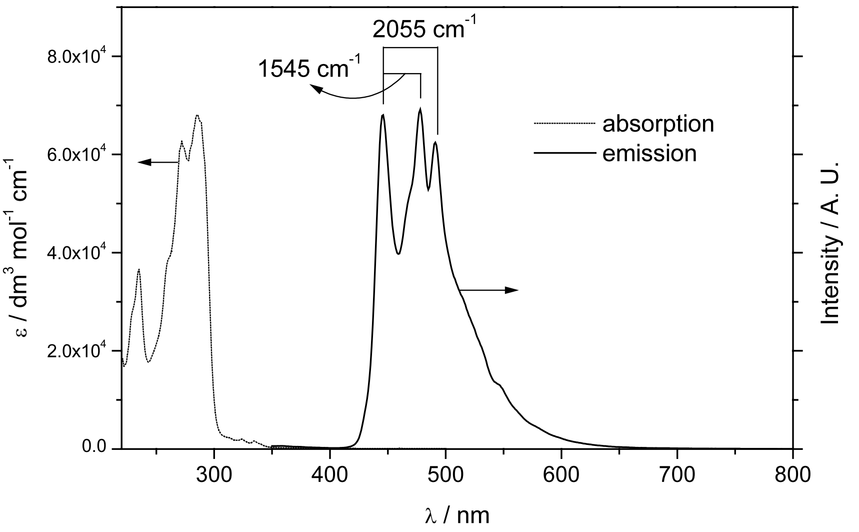

Fig. 4. Absorption and emission ($\lambda_{ex} = 297$ nm) spectra of **6** in CH_2Cl_2 solution (1.1×10^{-5} mol dm^{-3}) at 298 K.

ganic framework. The incorporation of $[Au(PCy_3)]^+$ moieties into these systems confers rich triplet characteristics for the radiative excited states through Au-induced spin–orbit coupling.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 194202 for the compound **3**·CH_2Cl_2. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-33603; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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