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Synthesis and photolysis of a new series of Cu(I) complexes with tri-*m*-tolylphosphine and heterocyclic thiones. The crystal structure of bis[μ-iodo(pyridine-2-thione)(tri-*m*-tolylphosphine)copper(I)]

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Abstract

Reactions of $[Cu(tmtp)I]_4$ (tmtp = tri-*m*-tolylphosphine) with heterocyclic thiones (L) (L = pyridine-2-thione (py2SH), pyrimidine-2-thione (pymtH), 1,3-thiazolidine-2-thione (tzdtH), 1-methyl-1,3-imidazoline-2-thione (meimtH), benz-1,3-imidazoline-2-thione ($bzimtH_2$) and quinoline-2-thione (qntH)) yield binuclear complexes of the general formula $[Cu(tmtp)(L)I]_2$. The complexes have been characterized by elemental analyses and their IR, UV–Vis and ^1H NMR spectroscopic data. The photolysis of these complexes in dichloromethane solutions has been investigated. The crystal structure of $[Cu(tmtp)(py2SH)I]_2$ has been determined by single-crystal X-ray diffraction methods. The orange crystals are triclinic, space group $P\bar{1}$ with $a = 9.9881(6)$, $b = 10.8255(5)$, $c = 13.5355(8)$ Å, $\alpha = 77.268(2)$, $\beta = 94.409(2)$, $\gamma = 68.102(2)°$, $D_{calc} = 1.543$ Mg m^{-3}, $V = 1303.94(2)$ Å^3 and $Z = 1$. The molecule contains a planar Cu_2I_2 moiety with Cu–I bond lengths of 2.690(1) and 2.695(1) Å. The Cu–P and Cu–S distances are 2.241(1) and 2.303(1) Å, respectively. The Cu$\cdots$Cu separation is 3.119(1) Å.

Introduction

Copper(I) complexes continuously attract considerable interest because of the importance of metal–metal interaction in d^{10} systems [1–3]. Along this line a vast amount of dimeric adducts with heterocyclic thiones as ligands have been structurally characterized [4–8].

In recent papers we have described the structure analysis of $[CuBr(PPh_3)(py2SH)]_2$ [9], $[CuCl(tptp)(pymtH)]_2$ and $[CuCl(tptp)(tzdH)]_2$ [11]. These complexes have been found to be dimeric with the thione ligand bridging two metal atoms. The photochemical behaviour of these complexes has also been investigated [10–12].

In order to investigate the experimental conditions employed in synthetic reactions and the possible transformation of the complexes following the elimination of phosphine upon photolysis we report on the synthesis and characterization (physical properties and photochemical behaviour) of a new series of complexes of the general formula $[Cu(tmtp)(L)I]_2$.

Experimental

Materials and instruments

Copper halides and tri-*m*-tolyphosphine (Merck) were used as obtained, while the thiones (Merck or Aldrich) were recrystallized from hot ethanol prior to their use. All solvents used were of reagent grade.

IR, electronic and NMR spectra, conductivities, magnetic susceptibility measurements and elemental analyses of carbon, nitrogen and hydrogen were performed as described previously [10].

The photolyses and quantum yields measurements were carried out in 1 cm quartz cells using a high pressure HBO 200W/4 Osram lamp, a 2 cm water filter and a monochromator manufactured by Applied Photophysics. All the photochemical work was carried out in the dark.

Preparation of the complexes

$[Cu(tmtp)I]_4$ was prepared by heating equimolar quantities of CuI and tmtp at 50–70 °C in acetonitrile, for about 30 min.

The complexes of the formula $[Cu(tmtp)(L)I]_2$ were prepared according to the following general

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procedure. A solution of 0.4 mmol of the appropriate thione in 20 ml of methanol was added to a solution of 0.1 mmol of $[Cu(tmtp)I]_4$ in 20 ml acetonitrile and the resulting solution was moderately heated for 30 min. It was then allowed to cool and the microcrystalline products were isolated. The compounds were identified by elemental analyses and by their IR, UV–Vis and NMR spectra.

Collection and reduction of intensity data

Complete crystal and intensity collection data are reported in Table 1. Preliminary oscillation and Weissenberg photographs indicated the space group $P\bar{1}$. Unit cell dimensions were derived from least-squares refinement of the setting angles of 30 automatically centered reflections in the range $23 < 2\theta < 53°$ on a Syntex $P2_1$ diffractometer upgraded by CRYSTAL LOGIC. The intensities of three standards monitored after every 97 reflections were stable a scatter of less than 3% from their respective means. The data were corrected for Lorentz–polarization and absorption effects.

TABLE 1. Summary of crystal and intensity collection data

Formula	$Cu_2I_2(SNC_5H_5)_2(PC_{21}H_{21})_2$
Formula weight	1212.00
a (Å)	9.9881(6)
b (Å)	10.8255(8)
c (Å)	13.5355(8)
α (°)	77.268(2)
β (°)	94.409(2)
γ (°)	68.102(2)
V (Å^3)	1303.94(2)
Z	1
D_{calc} (Mg m^{-3})	1.543
D_{meas} (Mg m^{-3})	1.53
Space group	$P\bar{1}$
Radiation	Cu Kα ($\lambda = 1.5418$)
μ (cm^{-1})	120.83
Scan speed (°/min)	4.5
Scan range (°)	1.9 plus $\alpha_1 - \alpha_2$
2θ limit (°)	130.0
Data unique	4676
Data used	4254
$F_o >$	6.0 $\sigma(F_o)$
R_{int}	0.0225
Range of hkl	$-11 \rightarrow 11$, $-12 \rightarrow 12$, $0 \rightarrow 15$
Weighting scheme	$1/w = \sigma^2(F_o) + 0.0005\ \lvert F_o \rvert^2$
$F(000)$	604
No. refined parameters	367
$\lvert \Delta/\sigma \rvert_{max}$	0.098
$(\Delta p)_{max}$ (e Å^{-3})	1.910
$(\Delta p)_{min}$ (e Å^{-3})	1.642
S[a]	3.81
R (obs.)[b]	0.0474
R (all data)[b]	0.0485
R_w (obs.)[c]	0.0642
R_w (all data)[c]	0.0647

[a] $S = [\Sigma w(\Delta F)^2/(N-P)]^{1/2}$, N = no. observed reflections, P = no. parameters. [b] $R = \Sigma \lvert \Delta F \rvert / \Sigma \lvert F_o \rvert$. [c] $R_w = [\Sigma w \Delta F)^2 / \Sigma w \lvert F_o \rvert^2]^{1/2}$.

Solution and refinement of the structure

The structure was solved by direct methods and refined by full matrix least-squares, in which $\Sigma w \Delta F^2$ was minimized using the SHELX76 [13] program. The hydrogen atoms were revealed by ΔF calculations except those of the methyl groups, calculated as riding on carbon at a distance of 1.08 Å. Non-hydrogen atoms were refined using anisotropic factors and hydrogen atoms using isotropic temperature factors. Atomic scattering factors were taken from the International Tables for X-ray Crystallography [14]. Positional parameters and the anisotropic thermal parameters of the non-H atoms are given in Tables 2 and 3; bond lengths and angles in Table 4.

TABLE 2. Positional parameters of non-H atoms with e.s.d.s in parentheses

Atom	x	y	z
I	10357.3(3)	8083.1(2)	4558.5(2)
Cu	8716.7(6)	817.6(6)	4067.7(4)
P	8863(1)	1949.7(9)	2507.6(7)
S	6558(1)	627(1)	4379.5(8)
C(1)	5140(4)	2177(4)	4234(3)
C(2)	5214(5)	3468(5)	3979(4)
C(3)	3974(7)	4671(5)	3812(5)
C(4)	2596(6)	4590(5)	3919(5)
C(5)	2573(5)	3326(5)	4195(4)
N	3783(4)	2195(4)	4354(3)
C(11)	8325(4)	1389(4)	1412(3)
C(12)	8599(5)	1832(4)	434(3)
C(13)	8206(5)	1378(4)	−375(3)
C(14)	7520(6)	478(5)	−204(4)
C(15)	7223(6)	43(6)	742(4)
C(16)	7629(5)	478(5)	1581(4)
C(17)	8509(7)	1899(6)	−1440(4)
C(21)	7680(4)	3793(4)	2166(3)
C(22)	8026(5)	4640(4)	2673(3)
C(23)	7107(5)	6023(4)	2514(3)
C(24)	5792(5)	6556(4)	1832(4)
C(25)	5416(5)	5705(5)	1328(3)
C(26)	6346(4)	4350(4)	1491(3)
C(27)	7545(9)	6912(6)	3046(6)
C(31)	10666(4)	1917(4)	2321(3)
C(32)	10872(5)	3002(5)	1678(3)
C(33)	12275(6)	2894(6)	1517(4)
C(34)	13453(5)	1678(6)	2014(4)
C(35)	13264(5)	611(6)	2660(4)
C(36)	11889(4)	713(4)	2823(3)
C(37)	12492(8)	4061(8)	830(6)

TABLE 3. Thermal parameters of non-H atoms with e.s.d.s in parentheses

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
I	48.1(2)	24.4(1)	48.6(2)	−11.3(1)	0.3(1)	−11.4(1)
Cu	43.0(3)	33.6(3)	40.9(3)	−16.1(3)	8.0(2)	−4.6(2)
P	33.1(4)	26.9(4)	34.0(4)	−11.4(4)	3.5(3)	−5.5(3)
S	35.3(5)	30.5(5)	61.7(6)	−12.6(4)	10.0(4)	−4.3(4)
C(1)	44(2)	35(2)	39(2)	−17(1)	10(1)	−8(1)
C(2)	60(2)	43(2)	69(2)	−26(2)	21(2)	−15(2)
C(3)	80(2)	37(2)	97(3)	−22(2)	31(2)	−15(2)
C(4)	70(2)	40(2)	96(3)	−7(2)	28(2)	−26(2)
C(5)	43(2)	55(2)	78(2)	−15(2)	21(2)	−23(2)
N	42(2)	34(2)	56(2)	−15(1)	13(1)	−12(1)
C(11)	37(2)	32(2)	43(2)	−8(1)	2(1)	−13(1)
C(12)	49(2)	32(2)	42(2)	−11(1)	4(1)	−11(1)
C(13)	49(2)	40(2)	41(2)	5(2)	−2(1)	−14(1)
C(14)	68(2)	53(2)	61(2)	−11(2)	−8(2)	−30(2)
C(15)	75(2)	60(2)	76(2)	−36(2)	0(2)	−26(2)
C(16)	59(2)	52(2)	50(2)	−30(2)	4(2)	−18(2)
C(17)	85(3)	71(2)	47(2)	−6(2)	12(2)	−20(2)
C(21)	40(2)	30(2)	35(2)	−13(1)	5(1)	−3(1)
C(22)	54(2)	34(2)	47(2)	−16(2)	−4(2)	−6(1)
C(23)	69(2)	36(2)	53(2)	−18(2)	1(2)	−10(2)
C(24)	62(2)	32(2)	59(2)	−4(2)	7(2)	−8(2)
C(25)	44(2)	51(2)	50(2)	−4(2)	−4(2)	−9(2)
C(26)	38(2)	41(2)	48(2)	−14(1)	4(1)	−18(1)
C(27)	131(3)	42(2)	112(3)	−33(2)	−10(3)	−27(2)
C(31)	34(2)	43(2)	33(1)	−16(1)	3(1)	−8(1)
C(32)	49(2)	59(2)	48(2)	−29(2)	9(2)	−2(2)
C(33)	61(2)	94(2)	56(2)	−50(2)	20(2)	−15(2)
C(34)	45(2)	93(2)	57(2)	−33(2)	15(2)	−28(2)
C(35)	38(2)	69(2)	61(2)	−11(2)	6(2)	−27(2)
C(36)	38(2)	45(2)	44(2)	−13(1)	4(1)	−16(1)
C(37)	88(2)	127(3)	109(3)	−71(2)	15(2)	21(3)

Results and discussion

All the prepared complexes are microcrystalline solids soluble in dichloromethane, chloroform, acetonitrile, ethanol, methanol and acetone. Their elemental analyses confirm their stoichiometry and their physical properties are in accordance with the proposed structures. Room temperature magnetic measurements on several species confirm that the central metal ion is diamagnetic Cu(I), while conductivity measurements reveal, as expected, a non-electrolytic nature.

Spectroscopy

The UV–Vis spectra of the complexes in dichloromethane are dominated by two main absorptions in the regions 250–260 and 280–3100 nm, respectively. The first band is ascribed to the intraligand transitions of the phosphine ligand for which two bands are observed at 245 and 260 nm, respectively, having log ϵ values (*c.* 4.1) similar to their counterparts in the complexes. The second band expresses a small red shift (10–20 nm) with respect to the corresponding one in the spectra of the free thiones. Therefore, this band, which is accompanied by a third one in the region 350–380 nm in the case of conjugated heterocyclic thiones, should be ascribed to the intraligand transitions of the thione ligand [15]. No shoulders are detected in the above-mentioned bands, therefore it cannot be unambiguously stated whether any MLCT transitions occur in the same region. In order to reveal any CT character of these bands, the electronic spectra were recorded also in toluene, tetrahydrofuran and acetonitrile. The thione originating absorption bands expressed a small blue shift (no more than 10 nm) on going to more polar solvents.

Note should be made at this point that the conflicting effects of the coordinated phosphine molecule and halogen atom are known to cause shift of the MLCT bands to lower [16] and higher [17] wavelengths, respectively. In view of this fact and of our observation we may conclude that the intraligand thione bands possess partial CT character.

IR spectra in the region 4000–250 cm^{-1} provide information concerning the coordination mode of

TABLE 4. Interatomic distances (Å) and angles (°)[a] for [Cu(tmtp)(py2SH)I]$_2$

Distances			
Cu–I	2.690(1)	C13–C14	1.377(7)
Cu–I	2.695(1)	C13–C17	1.523(7)
Cu–P	2.241(1)	C14–C15	1.357(8)
Cu–S	2.303(1)	C15–C16	1.408(6)
Cu–Cu	3.119(1)	C21–C22	1.382(6)
P–C11	1.828(4)	C21–C26	1.395(5)
P–C21	1.831(4)	C22–C23	1.390(6)
P–C31	1.826(4)	C23–C24	1.387(7)
S–C1	1.703(4)	C23–C27	1.486(7)
N–C1	1.371(5)	C24–C25	1.397(7)
C1–C2	1.395(6)	C25–C26	1.369(6)
C2–C3	1.380(7)	C31–C32	1.392(5)
C3–C4	1.428(8)	C31–C36	1.395(5)
C4–C5	1.347(7)	C32–C33	1.401(6)
C5–N	1.321(6)	C33–C34	1.379(8)
C11–C12	1.390(6)	C34–C35	1.370(7)
C11–C16	1.395(6)	C33–C37	1.370(7)
C12–C13	1.382(6)	C35–C36	1.375(6)
Angles			
I–Cu–P	113.3(0)	C12–C13–C17	119.8(5)
I–Cu–S	95.9(0)	C14–C13–C17	121.3(5)
P–Cu–S	120.3(0)	C13–C14–C15	120.9(4)
Cu–I–Cu	70.8(0)	C14–C15–C16	121.2(5)
Cu–P–C11	116.6(1)	C11–C16–C15	118.2(4)
Cu–P–C21	112.6(1)	P–C21–C22	119.4(3)
C11–P–C21	103.2(2)	P–C21–C26	121.9(3)
Cu–P–C31	116.4(1)	C22–C21–C26	118.2(4)
C11–P–C31	102.6(2)	C21–C22–C23	122.2(4)
C21–P–C31	103.7(2)	C22–C23–C24	118.5(4)
Cu–S–C1	113.5(1)	C22–C23–C27	120.5(5)
S–C1–C2	125.8(3)	C24–C23–C27	121.0(4)
S–C1–N	118.6(3)	C23–C24–C25	119.9(4)
C2–C1–N	115.6(4)	C24–C25–C26	120.5(4)
C1–C2–C3	121.1(4)	C21–C26–C25	120.6(4)
C2–C3–C4	119.3(5)	P–C31–C32	123.5(3)
C3–C4–C5	117.9(5)	P–C31–C36	117.6(3)
C4–C5–N	121.2(5)	C32–C31–C36	118.9(4)
C1–N–C5	124.8(4)	C31–C32–C33	121.2(4)
P–C11–C12	122.3(3)	C32–C33–C34	118.1(5)
P–C11–C16	118.2(3)	C32–C33–C37	121.0(5)
C12–C11–C16	119.5(4)	C34–C33–C37	120.9(5)
C11–C12–C13	121.3(4)	C33–C34–C35	121.2(4)
C12–C13–C14	118.9(4)	C34–C35–C36	120.9(4)
		C31–C36–C35	119.7(4)

[a] e.s.d.s. given in parentheses.

the ligands. Solid state IR spectra exhibit the dominance of the thione form of the ligands investigated deduced by the presence of ν(NH) bands at 3200–3130 cm^{-1} [18–20], the absence of any evidence for ν(SH) bands in the 2500–2600 cm^{-1} [21, 22] region and the production of characteristic 'thioamide bands' [21] as well as the characteristic medium ν(Cu–S) bands at 370–340 cm^{-1} [23].

The ^{1}H NMR spectra of the compounds in CDCl$_3$ solution at ambient temperature display, apart from the signals expected for the phosphine and thione ligands, a single resonance at $\delta \sim 11$–14 ppm attributed to the NH protons, thus confirming the prevalence of the thione tautomer in the complexes.

Description of the crystal structure

It is well known that Cu(I) has stereochemical preference for tetrahedral coordination. Recently we reported a series of binuclear copper(I) complexes where Cu(I) is four coordinate in the solid state [4, 8–11].

Fractional atomic coordinates and selected bond distances and angles are given in Tables 2 and 4, respectively. An ORTEP view of the molecule is given in Fig. 1. The molecule, which has a center of symmetry, is binuclear with two copper atoms joined by two iodine bridges. This is not unexpected because it is well known that monovalent oxidation states of coinage metals are typically soft acceptors strongly preferring soft ligands, such as iodine, and the steric effect is smaller. This can explain the difference that exists between the structure of [Cu(tmtp)(py2SH)I]$_2$ and the corresponding chlorine or bromine compounds such as [Cu(tptp)(pmtH)Cl]$_2$ and [Cu(PPh$_3$)(py2SH)Br]$_2$ [9–11]. Each copper atom is further coordinated to one S and one P atom, giving distorted tetrahedral coordination geometry around copper. The largest deviation from the ideal geometry, P–Cu–S = 120.3(0)°, may be attributed to steric interaction between the phosphine and thione ligands. The bridging iodine atoms and the two copper atoms form a planar rhombus with Cu–I distances of 2.690(1) and 2.695(1)°. The copper–copper separation is 3.119(1) Å.

The two Cu–P bond distances are 2.241(1) Å and are slightly longer than those found in other dimeric complexes with tetrahedral coordination around the copper atoms [9–11].

The observed Cu–S (2.303(1) Å) distances in the complex are shorter than those found in other bi-

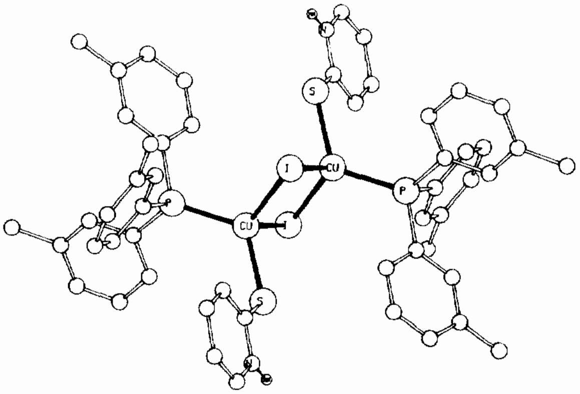

Fig. 1. A view of the complex.

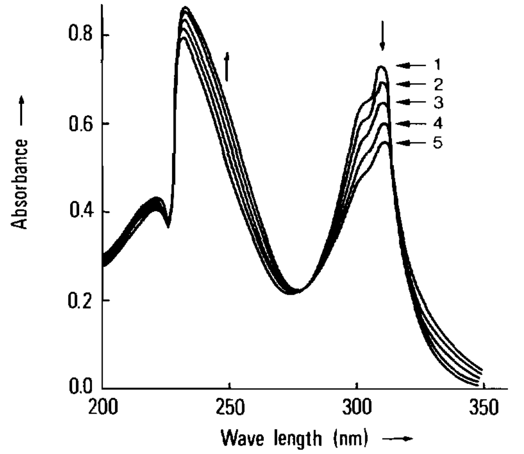

Fig. 2. UV absorption spectrum of a 2×10^{-5} M solution of $[Cu(tmtp)(bzimtH)I]_2$ in CH_2Cl_2 after irradiation at room temperature for (1) 0, (2) 10, (3) 20, (4) 30, (5) 40 min.

nuclear Cu(I) complexes with double bridging sulfur atoms, e.g. $[CuI(py2SH)_2]_2$ (2.328(1) and 2.577(2) Å) [8], $[Cu(py2SH)_3]Cl_2$ (2.298(3) and 2.538(4) Å) and $[Cu(py2SH)_3]Br_2$ (2.774(2) and 2.534(3) Å) [4]. In the case of $[Cu(PPh_3)(py2SH)Br]_2$ [9] the analogous bond lengths are 2.383(5) and 2.392(2) Å.

The Cu–I bond distances of 2.690(1) and 2.695(1) Å are similar to those found for tetrahedral Cu(I) complexes (2.527–2.728 Å) [24] with halogen bridges but are clearly longer than the corresponding distances in monomeric complexes with trigonal coordination around the Cu atom [7, 25, 26]. The bridging iodine atoms and the two copper atoms form a planar rhombus. The hydrogen S···H–N bridging bonds are N–H = 0.83(3) Å, H(N)···S = 2.48(3) Å and N···S = 3.408(4) Å.

Unexpectedly, the I–Cu–I and Cu–I–Cu angles, 109.2(2) and 70.8(3)°, respectively, do not agree with the predicted geometry for $Y_2MX_2MY_2$ dimers assumed by Summerville and Hoffmann for d^{10} systems (Cu–I–Cu = 94°), but they are exactly the calculated ideal values (109.5 and 70.5°) for a symmetric dimer [27]. Raper and co-workers observed in a series of centro-symmetric dimers with related ligands that opening up of the bridging Cu–S–Cu angle is accompanied by a shortening of the S···S separation and an increase of the metal–metal one, together with an elongation of the two Cu–S distances [7]. Contrariwise, in the compound described here, where iodine acts as the bridge atom, there is no remarkable difference from the corresponding values of monomeric complexes.

The Cu–P–C(11) and Cu–P–C(21) angles (116.6(1) and 112.6(1)°) are closer to the ideal tetrahedral value than those found in $[Cu(tptp)(pmtH)Cl]_2$ and $[CuCl(tptp)(tzdH)]_2$. The Cu–S–C angle (113.5(1)°) is not far from the tetrahedral value and it is bigger than those previously observed for coordinated py2SH molecules. The S–Cu–P angle 120.3(0)° differs from the ideal tetrahedral value because of the thione and phosphine steric repulsive effect.

Photolysis

Irradiation of dichloromethane solutions of the complexes at $\lambda_{exit} = 300$ nm at room temperature causes the decomposition of the complexes within minutes, without the evolution of new bands. A relevant representation of the spectral changes for $[Cu(tmtp)(bzimtH)I]_2$ during irradiation is depicted in Fig. 2. The decomposition of the complexes is not at all unexpected on the grounds of the lability of the triphenylphosphine ligand in solution [10–12, 28, 29].

Quantum yields have been determined at room temperature relative to potassium ferroxalate standard and are reported in Table 5.

Supplementary material

Lists of observed and calculated structure factors, of positional and anisotropic thermal parameters of the H atoms and of the positional and equivalent

TABLE 5. Some physical properties and analytical data of the complexes

Complex	Φ_i/Φ^{300} [a]	Colour	Melting point (°C)	Elemental analysis: found (calc.) (%)		
				C	H	N
$[Cu(py2SH)(tmtp)I]_2$ (**1**)	0.116	orange	165	51.84 (51.53)	4.10 (4.32)	2.17 (2.31)
$[Cu(pymtH)(tmtp)I]_2$ (**2**)	0.201	red	152	49.32 (49.47)	4.06 (4.15)	4.92 (4.61)
$[Cu(tztdH)(tmtp)I]_2$ (**3**)	0.081	yellow	145	47.22 (46.94)	3.90 (4.27)	2.00 (2.28)
$[Cu(meimtH)(tmtp)I]_2$ (**4**)	0.104	white	185	49.55 (49.30)	4.36 (4.46)	4.55 (4.60)
$[Cu(bzimtH_2)(tmtp)I]_2$ (**5**)	0.237	white	168	52.19 (52.14)	4.20 (4.22)	4.24 (4.34)
$[Cu(qntH)(tmtp)I]_2$ (**6**)	0.041	red	154	54.92 (54.92)	4.08 (4.30)	2.06 (2.13)

[a] Φ_i/Φ^{300} = quantum yield relative to potassium ferroxalate at 300 nm.

thermal parameters of the phenyl-carbon atoms are available from the authors on request.

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