OXIDATION OF METALLIC COPPER AND SILVER BY ORTHOQUINONES IN ORGANIC SOLVENTS

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It is known that o-quinones, which react actively with alkali metals in polar solvents, are also capable of oxidizing thallium, zinc, and cadmium [1, 2], forming o-semiquinolate complexes of the respective metal. The oxidation of metals having a negative redox potential can be realized in aprotic solvents with oxidizing agents having moderate strength, if it is realized in the presence of a complexing agent capable of stabilizing the metal cation and thereby raising the redox potential of the process. The recently proposed method for the synthesis of complexes of transition metals [3-5] was based on the oxidation of the metal by halides, alkyl halides, and other similar oxidizing agents in polar solvents of the DMFA, DMSO, acetonitrile, and benzonitrile types capable of being coordinated at the transition-metal cations. In this connection it seemed promising to use o-quinones, capable of acting simultaneously as oxidizing agent and complexing agent, for the dissolution of metals in or-ganic solvents.

The main condition for the reaction of the metals with o-quinones is the correspondence of the redox potentials of the reagents. Data on the redox potentials of substituted o-quinones in polar organic solvents are quite few and are contradictory [6-9], and this creates certain difficulties in the choice of o-quinone.

Earlier [10-11] we reported on the one-electron oxidation of the heavy metals copper, silver, and mercury by substituted o-quinones in solvating solvents in the presence of halide ions. More recently [12] it was shown that metallic copper and silver are oxidized by o-quinones in THF in the presence of the electron-donating ligand Ph_3P , which stabilizes the paramagnetic bis(triphenylphosphine)-o-semiquinolate complexes of Cu(I) or Ag(I) formed as a result of the reaction.

The aim of the present work was to investigate the effect of the nature of the o-quinone, the organic solvent, and various complexing additives on the dissolution of metallic copper and silver. For this purpose we studied the reactions of a series of o-quinones (Q) (Ia-k) with metallic copper and silver in hexane, toluene, and THF. As complexing components we used isonitriles, olefins, and 2,2'-bipyridyl,



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		(C6H11NC)2CuS	2		C ₆ H ₁₁ NCCuSQ	2	
SQ	g _i	A _{63,65} Cu	A _H (SQ)	Bi	A _{63,65} Cu	A _H (SQ)	
			Oe		Øe		
(IIa)	2,0065	10,0					
(IIb)	2,0098	10,1					
(IIc)	2,0051	7,5 8,4					
(IId)	2,0060	7,6 8,5					
(IIe)	2.0046	9,0	1,4(2H)	2,0028	5,0		
-(IIf)	2,0037	9,4	3,2(H)	2,0023	5,1	3,5(H)	
-(IIg.)	2.0038	9,3	3,1 (2H)	2,0022	5,0	3,4(2H)	
(11b)	2,0056	8,5	1		1		
(IIi)	2,0046	8,0	1,2(2H) 3,8(H)	2,0035	6,2		
(1Ij)	2,0047	7,8	1,6 (4H)	2,0038	3,6	1,8(4H)	
(1 I k)	2,0043	7,6	1,2(6H)	2,0031	4,2	1,4(6H)	

TABLE 1. The Parameters of the ESR Spectra of the Isonitrile-osemiquinolate Complexes of Cu(I) in Toluene

TABLE 2. Parameters of the ESR Spectra of the Isonitrile-o-semiquinolate Complexes of Ag(I) in Toluene

		(C ₆ H ₁₁ NC) ₂ AgSQ	2		C _s H ₁₁ NCAgSQ		
SQ	<i>g</i> .	A _{107,108} Ag	A _H (SQ)	gi	A107,108Ag	$A_{\mathrm{H}}(\mathrm{SQ})$	
		С	e	-	C)e	
(IIc)	2,0040	1,3				•	
(IIf)	2,0036	1,5	3,3(H)				
(IIg)	2,0033	1,5	3,1 (2H)				
(IJe)				2,0028	-	1,4(2H)	

The choice of ligands was determined by their ability to form complexes with the Cu and Ag ions and also their indifference with respect to the o-quinones (Ia-k). The last fact is of great importance, since interaction between the neutral ligand and the o-quinone (as occurs, for example, in the case of triphenylphosphine [12]) removes the reagents required for dissolution from the reaction, which leads to a very low yield of the desired products.

<u>Reaction of Copper with o-Quinones without Complexing Agents.</u> We showed that in the absence of oxygen compounds (Ia-h) react with metallic copper in all the listed solvents with the formation of the bis-o-semi-quinolate complexes of $Cu(\Pi)$ according to the equation:

$$Cu + 2Q = Cu(SO)_2 \tag{1}$$

where SQ is the anion of the respective o-semiquinone (IIa-k). In the reaction (1) of the bifunctional quinone (Ie) with copper in THF and in toluene the dark-blue crystalline mononuclear bis-o-semiquinolate complex $Cu(SQ)_2$ [where SQ = (IIe)], poorly soluble in the indicated solvents, was isolated.

The quinones (Ii-k) clearly have the lowest oxidation potentials of all the investigated quinones, and the oxidative addition of these quinones to metallic copper in the organic solvents does not take place even in the presence of such electron-donating additives as alkenes and 2,2'-bipyridyl.

In such reactions compounds (Ia, b) occupy a special position among the listed o-quinones. To judge from published data on the redox potentials of substituted o-quinones in aqueous media and also from the behavior in substitution reactions [12], these o-quinones have the highest oxidation potentials. In addition, compounds (Ia, b) have very reactive halogen atoms at positions 4 and 5, particularly in the semiquinone form. This facilitates nucleophilic substitution at the given carbon atoms, which leads under the conditions for the synthesis of the o-semiquinolate complex to secondary reactions in the ligand and, in particular, to the formation of the corresponding oxanthrenesemiquinone derivatives. Thus, in the reaction between metallic copper and compounds (Ia, b), irrespective of the nature of the solvent and the alkene addition, the final reaction product is not the corresponding bis-o-semiquinolate of Cu(II) but a mixture with the oxanthrene-o-semiquinolate derivatives having a quantitative preponderance of the latter:



 $X = Cl, \dot{B}r$

If reaction (1) is carried out in air, the atmospheric oxygen oxidizes the obtained $Cu(SQ)_2$ to the corresponding o-quinone and cupric oxide:

$$2\mathrm{Cu}(\mathrm{SQ})_2 + \mathrm{O}_2 \to 2\mathrm{CuO} + 4\mathrm{Q} \tag{3}$$

It was shown experimentally that a saturated solution of $Cu(SQ)_2$ [SQ = (IIf)] in acetonitrile at ~20°C absorbs 0.5 mole of oxygen in 3 h, and this leads to an almost quantitative yield of (If) and cupric oxide. Thus, when reaction (1) is carried out in a system where there are traces of oxygen the oxygen oxidizes the $Cu(SQ)_2$ at the moment of formation, and the cupric oxide formed as a result of oxidation passivates the surface of the metal, and the reaction stops. This explains the fact that reaction (1) was not detected earlier [10, 12].

The oxidation rate of metallic copper by the o-quinone depends both on the oxidation potential of the oquinone and on the nature of the solvent. Thus, for example, some increase in the rate is observed in the series hexane, toluene, THF. From comparison of the intensity of the λ 305-nm band in the electronic absorption spectra of the Cu(SQ)₂ formed in the reaction of copper with (If) it follows that with (If) at a concentration of 10^{-3} M at 20°C the substitution of hexane by toluene gives a 1.5-fold increase in the formation rate of Cu(SQ)₂₂ while substitution of hexane by THF leads to a 6-7-fold increase in the reaction rate. Such an increase in the dissolution rate of metallic copper leads to the possible role of THF as a complexing agent in this reaction.

Reaction of Copper with o-Quinones in the Presence of Complexing Agents. When reaction (1) is realized in toluene, the addition of catalytic amounts (5 mole % in relation to the o-quinone) of such weak electron donors as olefins (styrene, 1,5-cyclooctadiene) gives rise to an increase in the dissolution rate of metallic copper by 30-40 times. In the presence of olefins such as styrene the reaction takes place through the formation of an alkene-o-semiquinolate complex of Cu(I), the weak ESR signal of which ($g_i = 2.0031$, $A_{Cu} = 5.2$ Oe, $A_H = 3.4$ Oe) is observed in the solution during the reaction:

$$Cu + (Ie) + Alken \rightarrow Alken \cdot CuSQ$$
(4)

$$2\text{Alken} \cdot \text{CuSQ} \rightleftharpoons \text{Cu(SQ)}_2 + 2\text{Alken} + \text{Cu}$$

$$SQ = (IIf)$$
(5)

The use of neutral electron-donating additives (isonitriles, 2,2'-bipyridyl, o-phenanthroline, and alkenes) makes the oxidative addition of o-quinones to metallic copper a convenient preparative method for the production of o-semiquinolate and catecholate complexes of copper. The composition and electronic structure of the obtained complexes of copper depend both on the oxidation potential of the corresponding o-quinone, which is capable of

coordinating at the metal atom in three different oxidation-reduction states $Q \xrightarrow{+e} SQ \xrightarrow{+e} Cat$ [where Cat is the cation of the respective catechol $(\Pi a-k)$ and on the nature of the electron-donating substituent, its basicity, the steric factors, etc.

The use of isonitriles as n-donating ligand leads to the formation of a series of bis(isonitrile)-o-semiquinolate complexes of Cu(I):

$$Cu + Q + 2RNC \rightarrow (RNC)_2 CuSQ \tag{6}$$

where R = phenyl, tert-butyl, or cyclohexyl.

The isonitrile reduces the redox potential of the metal, and the copper reacts even with compounds (Ii-K). The parameters of the ESR spectra of the isonitrile-o-semiquinolate complexes of Cu(I) are given in Table 1. The g factors and the splitting constants at the copper isotopes ⁶³Cu and ⁶⁵Cu for these complexes in toluene are close to those given in [12] for the bis(triphenylphosphine)-o-semiquinone complexes of Cu(I). Most of the bis-(isonitrile)-o-semiquinolate complexes of Cu(I) listed in Table 1 were isolated individually with good yields. The replacement of one isonitrile by another has practically no effect on the parameters of the ESR spectra. However, the elimination of one molecule of the isonitrile as a result of the dissociation of the complex leads to considerable changes in the splitting constants at the Cu isotopes and in the proton constant at the o-semiquinolate ligand. The ESR spectra of the bis(isonitrile)-o-semiquinolate complexes of Cu(I) at 78°K have not yet been interpreted.

Reaction (6) goes not only in solvating solvents but also in toluene, hexane, etc., and the excess of metallic copper in the reaction with (If, g) in the presence of t-BuNC leads to the disappearance of the ESR signal of (t-BuNC)₂CuSQ in the solution and to the formation of a nonparamagnetic product, which probably contains the o-quinone in the two-electron reduced form in the form of a dianion, during the oxidation of which in solution by atmospheric oxygen the ESR signal of the corresponding bis(isonitrile)-o-semiquinolate complex of Cu(I) re-appears [13].

To judge from the oxidation reactions of mercury in THF in the presence of lithium chloride [14] and also from the substitution reactions of other o-quinones in the o-semiquinolate complexes of Cu(I), the oxidation potential of (Ie) is close to that of (If, g). The formation of a biradical derivative in reaction (6) should be expected from this bis (o-quinone). The synthesized compound represented a thermally unstable oil and was not isolated individually. The low-temperature ESR spectrum of this complex at 79°K in toluene was similar to the spectra of the mononuclear derivatives (IIf, g). In the half-field region at 79°K there was no singlet line characteristic of the biradical derivative in the spectrum [14]. This can be interpreted as the absence of the biradical derivative, explained by the steric hindrances to its formation. The ESR spectrum of (cyclo- $C_{6}H_{11}NC)_{2}CuSQ$ [SQ = (IIe)] in solution at ~20°C is due to the coupling of the unpaired electron with the Cu isotopes and has additional splitting with constant A=1.4 Oe and intensity ratios of 1:2:1. The absence of this splitting in the corresponding bis(radical-anion) made it possible to suppose that it was due to the pair of equivalent protons in the n-donor ligand. Substitution of the n-donor ligand cyclo- $C_6H_{11}NC$ by t-BuNC, PPh₃, or $P(OR)_3$ does not lead to the disappearance of the splitting or to a change in the value of the constant, and this provides the basis for the assertion that it is due to the H^d and H^c protons of the o-semiquinolate ligand (Fig. 1). The larger value of the splitting constant at the H^d and H^c atoms compared with the proton constant at the tertbutyl groups in (Ig, h), equal to 0.3 Oe, is explained both by the transfer of spin density along the two bonds of the σ core of the molecule and by increase in the contribution from the spin-polarization mechanism in connection with the fact that both protons fall outside the plane of the chelate unit, where this contribution in the given complex is clearly significantly larger than in the corresponding bis(radical-anion).

The reaction of metallic copper with o-quinones in the presence of such bifunctional n-donor compounds as 2,2'-bipyridyl and o-phenanthroline leads to the formation of complexes of Cu(II). Thus, compounds (Ic-f) react with metallic copper in all the above-mentioned solvents with the formation of the catecholate complexes of Cu(II) first synthesized in [15]. The above-mentioned o-quinones in reaction (7) are reduced by a two-electron mechanism to the corresponding dianions. As a result of the reaction of (Ie) with copper in toluene in the presence of additives of such a type dark-blue binuclear products moderately soluble in organic solvents are formed. Their elemental composition corresponds to the formula Cat_vCuL_2 [Cat = (IIIe)].



In order to assess the effect of the complexing additive on the dissolution rate of metallic copper we undertook a series of experiments on the dissolution of copper in a toluene solution containing (If) and the additives. According to the obtained data, all the additives can be arranged in the following order according to their effectiveness in increasing the dissolution rate of copper: RNC > 1,5-cyclohexadiene > styrene > 2,2'-bipyridyl > ophenanthroline.

The thermal dissociation of the bis(isonitrile)-o-semiquinolate complexes of Cu(I) leads to the formation of metallic copper, the corresponding isonitriles, and o-quinones:

$$(RNC)_{2}CuSQ \stackrel{70^{\circ}}{\rightleftharpoons} RNC + RNCCuSQ \stackrel{180^{\circ}}{\rightleftharpoons} 2RNC + Cu + Q$$
(8)

If the thermal dissociation is realized in solution in a degassed sealed tube, i.e., under conditions which exclude the withdrawal of the thermal dissociation products, the initial $(RNC)_2CuSQ$ is formed almost quantitatively when the solution is cooled. The ESR-spectroscopic control of the thermal dissociation of $(RNC)_2CuSQ$ [SQ = (IIf)] in xylene in the range of temperatures between 50 and 70°C showed superimposition of

the second s	Semiquinol- ate anion of	mp, °C	Molecular		Found/	calculated, η_0		
	dianion	(decomp.)	formula	c	Ħ	CI of Br	Сu	N
(C ₆ H ₁₁ NC) ₂ CuSQ	(11d)	73–75	C26H22Br6CuN2O4	32,41/32,16	2,43/2,27	49,37/49,48	7,17/7,06	3,01/3,09
(C ₆ H ₁₁ NC) ₂ CuSQ	(IIf.)	68-70	$C_{28}H_{42}CuN_2O_2$	66,62/66,93	8,58/8,37	1	12,32/12,75	5,87/5,58
(C ₆ H ₁₁ NC) ₂ CuSQ	(IIg)	68-70	C28H42CuN2O2	65,63/66,93	8,27/8,37	I	12,48/12,75	5,78/5,58
(C ₆ H ₁₁ NC) ₂ CuSQ	(111)	60-62	$C_{24}H_{28}CuN_2O_2$	63,43/65,45	6,70/6,36	I	14,02/14,55	6,92/6,36
(C ₆ H ₁₁ NC) ₂ CuSQ	(i II)	6365	$\mathrm{C}_{28}\mathrm{H}_{30}\mathrm{CuN}_{2}\mathrm{O}_{2}$	67,23/68,57	6,31/6,12	1	12,83/13,06	6,35/5,7
(C ₆ H ₁₁ NC) ₂ CuSQ	(IIk)	61 - 64	$\mathrm{C}_{22}\mathrm{H}_{30}\mathrm{CuN}_{2}\mathrm{O}_{4}$	62,87/62,26	6,82/6,60	1	14,93/15,09	6,90/6,60
$Cu(SQ)_2$	(IIc)	134 - 136	C ₂₄ Cl ₁₂ CuO ₈	31,57/31,79	1	47,12/47,01	6,96/7,06	
$Cu(SQ)_2$	(PII)	134 - 136	C24Br12CuO8	21,03/20,00	1	66,17/66,66	4,27/4,44	I
$Cu(SQ)_2$	(IIe)	125-127	$C_{42}H_{40}CuO_8$	69,32/68,47	5,58/5,43	ł	8,61/8,69	ł
$Cu(SQ)_2$	(II)	120-123	$C_{28}H_{4.0}CuO_4$	66,75/66,66	7,86/7,94	I	12,30/12,70	ł
$Cu(SQ)_2$	(IIg.)	120 - 123	$C_{28}H_{40}CuO_4$	66,85/66,66	7,73/7,94		12,54/12,70	I
dipy · Cu (Cat)	(IIIc)	142-144	C22H&Cl6CuN2O4	42,29/41,19	2,05/1,26	33,38/33,23	9,65/9,98	4,79/4,37
dipy-Cu(Cat)Cu-dipy	(IIIe) †	137-139	$C_{44}H_{36}Cu_2N_4O_4$	66,25/66,35	5,52/5,07	1	14,82/14,74	6, 39/6, 45
dipy · Cu (Cat)	(IIIf.)	135-137	$C_{24}H_{28}CuN_2O_2$	64,65/65,45	6,34/6,36	ŀ	14,63/14,54	6,48/6,36
phen · Cu (Cat)	(IIIg)	130-132	C ₂₆ H ₂₈ CuN ₂ O ₂	69,17/69,03	6,73/6,19	1	14,07/14,15	6,17/6,19

TABLE 3. Melting Points and Elemental Analyses of the Synthesized Compounds

* dipy = 2,2'-bipyridyl; phen = 1,10-phenanthroline. † The corresponding tetraanion.



 $(RNC)_2CuSQ, SQ = (IIe).$

the signals for the respective $(RNC)_2CuSQ$ and RNCCuSQ in the spectrum. In the solution at 70°C only the signal of one RNCCuSQ remains, and its intensity decreases with further increase in temperature and is practically equal to zero at 130°C.

The irradiation of solutions of 2,2'-bipyridyl- and o-phenanthrolinecatecholate complexes of Cu(II) by UV light with λ 300-400 nm, like heating to 140°C, leads to the reversible reaction:

$$\operatorname{CatCu} \cdot \operatorname{dipy} \stackrel{hv, \Delta}{\longleftrightarrow} \operatorname{dipy} + \operatorname{Cu} + Q \tag{9}$$

Oxidative Addition of o-Quinones to Metallic Silver. Metallic silver does not react with o-quinones (Ia-k) in the presence of such complexing additives as 2,2'-bipyridyl, o-phenanthroline, and alkenes. However, in the presence of isonitriles certain o-quinones oxidize metallic silver with the formation of paramagnetic isonitrile-o-semiquinolate complexes of Ag(I) in the solution (Table 2).

$$Ag + Q + 2RNC \xrightarrow{}_{hv, \Delta} (RNC)_2 AgSQ$$
 (10)

The parameters of the ESR spectra of the o-semiquinolate derivatives for the quinones (Id, f, g) formed in reaction (10) are close to the values obtained for the bis(triphenylphosphine)-o-semiquinolate derivatives of Ag(I) [12]. For the isonitrile complexes of these three o-quinones, as for the triphenylphosphine analogs described in [12], it was **not** possible to detect the signals of the monoisonitrile-o-semiquinolate complexes. In contrast to these results, the ESR spectrum of the isonitrile derivative (Ie), which differs from the spectra of the other isonitrile complexes in the absence of splitting at the ¹⁰⁷Ag and ¹⁰⁸Ag isotopes, can be interpreted as the spectrum of a monoisonitrile complex of Ag(I) [12, 16]. The impossibility of synthesizing the corresponding bisisonitrile derivative is clearly due to steric hindrances to its formation. The extreme instability of the synthesized (RNC)₂CuSQ [SQ = (IIe)] can be explained by the same reason.

All the known isonitrile-o-semiquinolate complexes of Ag(I) are thermally unstable. The intensity of the ESR signals of these complexes in solution decreases even at ~20°C, and the thermal stability decreases with substitution both of the isonitrile in the series of t-BuNC > $C_{6}H_{11}NC$ > PhNC and of the o-semiquinolate fragment in the series (IIf) > (IIg) > (IId) > (IIe).

The sensitivity of the solutions of all the isonitrile-o-semiquinolate complexes of Ag(I) to light should be noted. Thus, when the synthesis is realized in the light, the concentration of the paramagnetic $(RNC)_2AgSQ$ begins to increase only after the walls of the tube have been coated with metallic silver. Such light and heat sensitivity in the product hinders its isolation, and these compounds were therefore only investigated in solution by the ESR method. The order of the photosensitivity in the complexes which were investigated in solution corresponds to the order of their thermal instability.

EXPERIMENTAL

All the reactions were carried out in an inert atmosphere or under vacuum. The ESR spectra were recorded on an RÉ-1301 ESR spectrometer. The electronic spectra were recorded on an SF-16 instrument. The metals for dissolution were in the form of wires with a diameter of 0.6 mm.

<u>Bis(cyclohexylisonitrile)-3,5-di-tert-butyl-1,2-benzosemiquinolatecopper.</u> To a solution containing 4.4 g (20 mmole) of (If) and 4.5 ml (50 mmole) of cyclohexyl isocyanate in 50 ml of toluene we added 1.28 g (20 mmole) of metallic copper. The solution was stirred for several hours at ~20°C. The color of the solution became redbrown, and a dark-brown crystalline product separated. The solution was evaporated under vacuum at 20°C to

25 ml and cooled to 0°C. The precipitate was filtered off and dried under vacuum at 20°C for 2 h. The yield was ~100%; mp 70°C (decomp.). The elemental analyses are given in Table 3. The analogous derivatives of the other o-quinones were synthesized by a similar method.

Bis $(3,5-di-tert-butyl-1,2-benzosemiquinolate) copper (II) Cu(SQ)_2$. To a solution containing 4.4 g (20 mmole) of (If) and 0.1 ml (1 mmole) of styrene in 50 ml of toluene we added 5 g of metallic copper. The mixture was heated to 80°C and stirred for 12 h. The solution acquired a dark-blue color, and a dark-blue crystalline product separated. The precipitate was separated from the unreacted copper, filtered off, and dried under vacuum at 50°C. The yield in (If) was ~100%.

(3,5-Di-tert-butyl-1,2-catecholate)-2,2'-bipyridylcopper(II). The compound was obtained by the addition of an excess of metallic copper to a toluene solution containing 4.4 g (20 mmole) of (If) and 3.12 g (20 mmole) of 2,2'-bipyridyl in 50 ml of toluene. The mixture was heated to 80°C and stirred for 10 h and was then cooled to ~20°C. The dark-blue crystalline precipitate was separated from the unreacted metallic copper, filtered off, and dried under vacuum at 50°C for 6 h. The yield was ~100%. The elemental analyses are given in Table 3.

Effect of the Solvent on the Formation Rate of $Cu(SQ)_2$ [SQ = (IIf)] in Reaction (1). In a flask fitted with a magnetic stirrer we placed a spring of copper wire with a diameter of 0.6 mm. We then added the stoichiometric amount of a 10^{-3} M solution of (If) in hexane, toluene, or THF. The amount of $Cu(SQ)_2$ formed was determined by spectrophotometry. The effect of additions of styrene was determined in a similar manner.

In order to determine the effects of other complexing additives on the dissolution rate of metallic copper the copper samples were dissolved in a tenfold excess of a 0.2 M toluene solution of (If) and the respective additive. The reaction rate was determined as a function of the variation in the weight of the sample. All the reactions were carried out at 10°C.

The products from reaction (2) were analyzed qualitatively by spectroscopy (ESR) by the conversion of the bis (o-semiquinolate) complexes of Cu(II) into the corresponding mono-o-semiquinolate bisnitrile complexes of Cu(I). For this purpose the reaction mixture was separated from the metallic copper, and an excess of the isonitrile was added.

CONCLUSIONS

1. The oxidative addition of substituted o-quinones to metallic copper and silver in organic solvents was investigated. The effect of the nature of the o-quinone, the organic solvent, and the complexing additives (o-phenanthroline, 2,2'-bipyridyl, isonitriles, and alkenes) on the reaction was investigated.

2. The investigated dissolution reactions of metallic copper provide a convenient method for the production of the o-semiquinolate and catecholate complexes of Cu(I) and Cu(II) in preparative quantities.

3. The reversible photodissociation and thermal dissociation of the series of synthesized compounds in solution were investigated.

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