

行政院國家科學委員會專題研究計畫成果報告

1. 鹵醯類化合物之溶離反應及氧17核磁共振研究(二)  
(Solvolysis and Oxygen-17 NMR Studies of Acyl Halides II)
2. 錯鹽性液晶之合成研究(二)  
(Synthesis of Metal Complex Liquid Crystals II)

計畫類別：個別型計畫 整合型計畫

計畫編號：NSC 89-2113-M002-012

執行期間：88年8月1日至89年7月31日

計畫主持人：劉廣定

共同主持人：

處理方式：可立即對外提供參考

一年後可對外提供參考

兩年後可對外提供參考

(必要時，本會得展延發表時限)

執行單位：國立臺灣大學化學系

中華民國89年10月30日

# 摘 要

上年度完成之工作但在本年度整理完竣，以及在本年度完成之工作，其中有已投稿者，包括：

- (一) 苯甲醯溴溶離反應之溶劑效應及溶劑離子化能力  $Y_{\text{BnBr}}$  之應用 (附件一);
- (二) 苯甲醯氯之氧 17 核磁共振研究 (附件二);
- (三) 立體效應與 $\beta$ -雙酮錯合物之液晶性質 (附件三);

其餘尚在整理及待補充者包括：苯甲醯溴之氧 17 核磁共振化學移差，取代基效應與 $\beta$ -雙酮錯合物之液晶性質等亦將報告。

關鍵詞：氧17核磁共振，溶離反應，取代基效應，溶劑效應， $Y_{\text{BnX}}$  和 $Y_{\text{xBnX}}$  值，苯甲醯溴，密度泛函理論計算， $\beta$ -雙酮錯合物，液晶。

## ABSTRACT

The following results were completed in this year, or were partly done last year. Those were submitted for publication including:

- (1) Solvent and substituent effects on the solvolysis of benzoyl bromides, and Grunwald-Winstein correlation analysis with  $Y_{\text{BnBr}}$  scale. (Appendix 1).
- (2) Density functional theory calculations of O-17 and C-13 NMR chemical shifts for aromatic acyl chlorides. (Appendix 2);
- (3) Steric effect on the formation of columnar phases in  $\beta$ -diketonate copper(II) complexes. (Appendix 3).

Other results are to be completed next year including: the study on nmr chemical shifts for benzoyl bromides, substituent effects on the preparation of  $\beta$ -diketonate complexes and their mesomorphic properties will also be reported.

Keywords:

Oxygen-17 NMR, solvolysis, substituent effect, solvent effect,  $Y_{\text{BnCl}}$  and  $Y_{\text{BnBr}}$  values, DFT calculations, aromatic acyl bromides,  $\beta$ -diketonate complex, liquid crystals.

## ANNUAL REPORT (1999-2000)

The following results were completed and submitted for publication:

1. 4-Methoxy-, 4-methyl-, unsubstituted and 4-chlorobenzoyl bromides were prepared and solvolysis in a variety of solvents was studied. The linear  $\log k - Y_{\text{BnBr}}$  plots for 4-methoxy derivative indicates limiting  $S_{\text{N}}1$  mechanism, whereas the splitting of lines for nucleophilic solvents and poorly nucleophilic solvents in the case of 4-methyl derivative suggested nucleophilic solvent participation. The mechanism for the solvolysis of unsubstituted benzoyl bromide and 4-chlorobenzyl bromide probably varies with solvents, similar to that of the corresponding chlorides. Good linear Hammett  $\log k - \sigma^+$  plot could be found in a few solvents. It was submitted for publication.
2. Density functional theory at the level of B3LYP/6-31+G(d) was used to calculate chemical shifts of O-17 and C-13 of the carbonyl group of a variety of aromatic acyl chlorides, including phenyl, substituted phenyl, naphthyl, furyl and thienyl derivatives. The experimental values, which were observed last year, were used for comparison. The calculated O-17 chemical shifts correlated well with the experimental values and with Hammett-type  $\sigma^+$  constants. Therefore, in many cases it is possible to deduce  $\sigma^+$  constants of substituent or substituted aryl groups via calculation of O-17 chemical shifts of the carbonyl groups in gas phase. The  $\sigma^+$  constants so-obtained show the intrinsic property of substituents, so they provide a good reference set for systematic comparison to evaluate the effect of environment. Furthermore, the concept of  $n-\pi^*$  transition can be used to understand the sensitivity of O, Cl atoms and insensitivity of C atom towards substituent effects in aromatic acyl chlorides. (Appendix 2)
3. A systematic study of the mesomorphic properties of three series of copper(II) complexes based on  $\beta$ -diketonate ligands containing branched side chains was carried out. These disc-like compounds have four, six and eight flexible alkoxy side chains appended to the central core, in which two or four side chains were substituted by bulkier secondary alkoxy groups: 1-methylbutoxy or 1-methylheptoxy. The mesomorphic results indicated that at least eight side chains are required to form stable columnar mesophases; other compounds with four or six side chains were all non-mesogenic regardless of the combination of carbon chain length on the alkoxy groups of the side chains. If the diketonate ligand was 1-(3,4,5-trialkoxyphenyl)-3-(4-methylbutoxy)propane 1,3-dione, the complex was non-mesogenic. However, the presence of a longer 3-(4-methylheptoxy) side chain could make the complex to exhibit columnar phase if the trialkoxyphenyl group contained side chains of 6-12 carbons. The mesophases were characterized and identified as columnar hexagonal phases by thermal analysis and optical polarized microscopy. The presence of the introduced secondary alkoxy groups obviously appeared to influence the formation of columnar phases. The clearing points were relatively lower than similar copper(II) complexes not substituted by secondary alkoxy side chains. (Appendix 3)

Other results are:

1. The measurement of O-17 and C-13 chemical shifts in carbon tetrachloride

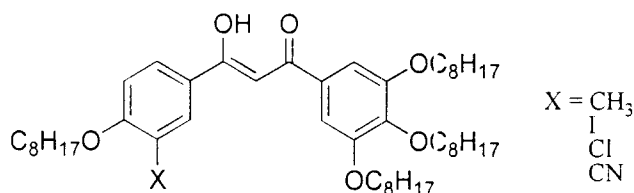
solution and the calculation of Mulliken charge distributions at B3LYP/6-31G(d) level. (Table 1)

Table 1

ArCOBr	$\delta$ , ppm (calcd)	$\delta$ , ppm (obsd)	$\Delta\delta$	$\sigma^+$	Charge (O)	Charge (C)
4-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	507.8	505.2	+2.6	-0.778	-0.385	+0.352
4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	517.8	518.0	-0.2	-0.311	-0.379	+0.355
C <sub>6</sub> H <sub>5</sub>	524.1	522.2	+1.9	0	-0.376	+0.357
4-ClC <sub>6</sub> H <sub>4</sub>	524.8	523.9	+0.9	+0.114	-0.375	+0.358
3-ClC <sub>6</sub> H <sub>4</sub>	531.1	528.5	+2.6	+0.399	-0.373	+0.360
4-CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	536.9	535.5	+1.4	+0.612	-0.371	+0.361

## 2. Synthesis of 3''-substituted $\beta$ -diketonate ligands and preparation of complexes

### (1) Synthesis of ligands



From substituted acetophenone, 3,4,5-trialkoxybenzoate and sodium hydride (NaH) in tetrahydrofuran solution under reflux the following ligands were made:

**(CH<sub>3</sub>-Ligand)**: 1-(3',4',5'-Trioctyloxyphenyl)-3-(3''-methyl-4''-octyloxyphenyl)propane 1,3-dione. A red, viscous liquid in 62% yield.

<sup>1</sup>H-NMR (ppm, CDCl<sub>3</sub>):

$\delta = 0.88$  (m, 12H, CH<sub>3</sub> in OR group),  $\delta = 1.27-1.84$  (m, 48H, -(CH<sub>2</sub>)<sub>24</sub> in OR group),  $\delta = 2.26$  (s, 3H, Ar-CH<sub>3</sub>),  $\delta = 3.99-4.06$  (m, 8H, -(OCH<sub>2</sub>)<sub>4</sub> in OR group),  $\delta = 6.66$  (s, 1H, OHC=CH for keto = enol form),  $\delta = 6.84$  (d, 1H, ArH),  $\delta = 7.16$  (s, 2H, ArH),  $\delta = 7.76$  (s, 1H, ArH),  $\delta = 7.80$  (d, 1H, ArH)

<sup>13</sup>C-NMR (ppm, CDCl<sub>3</sub>):

$\delta = 14.01$  (CH<sub>3</sub> in OR group),  $\delta = 16.23$  (Ar-CH<sub>3</sub>),  $\delta = 22.61, 26.04, 29.12, 29.19, 29.25, 29.33, 29.47, 30.30, 31.78, 31.84$  (C in OR group excluding -OCH<sub>2</sub>-),  $\delta = 68.08, 69.31, 73.46$  (-OCH<sub>2</sub>-),  $\delta = 91.78$  (COCH<sub>2</sub>CO),  $\delta = 105.89, 110.17, 126.94, 129.45$  (CH in Ar),  $\delta = 142.10, 153.01, 160.93$  (Aromatic C-OR),  $\delta = 126.81$  (Aromatic C-CH<sub>3</sub>),  $\delta = 127.06, 130.66$  (Aromatic C-COCH<sub>2</sub>CO),  $\delta = 184.66, 185.00$  (C=O)

IR (cm<sup>-1</sup>, Nujol) : 2960, 2928, 2858, 1607, 1462, 1379, 1342, 1261, 1135, 791, 723

HRMS (FAB) : Calcd for MH<sup>+</sup> C<sub>48</sub>H<sub>79</sub>O<sub>6</sub> 751.5876, found 751.5865

**(Cl-Ligand)** : 1-(3',4',5'-Trioctyloxyphenyl)-3-(3''-chloro- 4''-octyloxyphenyl)propane 1,3-dione

A red, viscous liquid in 52% yield.

<sup>1</sup>H-NMR (ppm, CDCl<sub>3</sub>) :

δ = 0.86 (m, 12H, CH<sub>3</sub> in OR group), δ = 1.27-1.88 (m, 48H, -(CH<sub>2</sub>)<sub>24</sub> in OR group), δ = 3.97-4.11 (m, 8H, -(OCH<sub>2</sub>)<sub>4</sub> in OR group), δ = 6.61 (s, 1H, OHC=CH for keto = enol form), δ = 6.95 (d, 1H, ArH), δ = 7.15 (s, 2H, ArH), δ = 7.85 (dd, 1H, ArH), δ = 7.98 (d, 1H, ArH)

<sup>13</sup>C-NMR (ppm, CDCl<sub>3</sub>) :

δ = 13.94 (CH<sub>3</sub> in OR group), δ = 22.56, 25.80, 25.99, 26.02, 28.84, 29.10, 29.20, 29.31, 29.43, 30.29, 31.69, 31.74, 31.80 (C in OR group excluding -OCH<sub>2</sub>-), δ = 69.16, 69.22, 73.38(-OCH<sub>2</sub>-), δ = 91.72 (COCH<sub>2</sub>CO), δ = 105.82, 112.14, 127.09, 128.95 (CH in Ar), δ = 142.31, 152.98, 157.73 (Aromatic C-OR), δ = 123.00 (Aromatic C-Cl), δ = 128.26, 130.08 (Aromatic C-COCH<sub>2</sub>CO), δ = 183.25, 184.96 (C=O)

IR (cm<sup>-1</sup>, Nujol) : 2957, 2929, 2859, 1598, 1495, 1465, 1380, 1337, 1271, 1194, 1117, 1060, 1017, 786, 723, 698

HRMS (FAB) : Calcd for MH<sup>+</sup> C<sub>47</sub>H<sub>76</sub>O<sub>6</sub><sup>35</sup>Cl 771.5330, found 771.5350

**(I-Ligand)** : 1-(3',4',5'-Trioctyloxyphenyl)-3-(3''-iodo- 4''-octyloxyphenyl)propane 1,3-dione

A red, viscous liquid in 80% yield.

<sup>1</sup>H-NMR (ppm, CDCl<sub>3</sub>) :

δ = 0.86 (m, 12H, CH<sub>3</sub> in OR group), δ = 1.27-1.87 (m, 48H, -(CH<sub>2</sub>)<sub>24</sub> in OR group), δ = 4.00-4.08 (m, 8H, -(OCH<sub>2</sub>)<sub>4</sub> in OR group), δ = 6.60 (s, 1H, OHC=CH for keto = enol form), δ = 6.82 (d, 1H, ArH), δ = 7.15 (s, 2H, ArH), δ = 7.93 (dd, 1H, ArH), δ = 8.37 (d, 1H, ArH)

<sup>13</sup>C-NMR (ppm, CDCl<sub>3</sub>) :

δ = 13.99 (CH<sub>3</sub> in OR group), δ = 22.59, 25.93, 26.00, 26.04, 28.85, 29.13, 29.17, 29.22, 29.32, 29.44, 30.30, 31.71, 31.75, 31.82 (C in OR group excluding -OCH<sub>2</sub>-), δ = 69.33, 69.40, 73.45 (-OCH<sub>2</sub>-), δ = 91.86 (COCH<sub>2</sub>CO), δ = 105.97, 110.91, 128.94, 138.33 (CH in Ar), δ = 142.37, 153.02, 160.74 (Aromatic C-OR), δ = 86.49 (Aromatic C-I), δ = 129.43, 130.20 (Aromatic C-COCH<sub>2</sub>CO), δ = 183.17, 184.98 (C=O)

IR (cm<sup>-1</sup>, Nujol) : 2958, 2923, 2858, 1593, 1462, 1379, 1341, 1265, 1117, 791, 724

HRMS (FAB) : Calcd for MH<sup>+</sup> C<sub>47</sub>H<sub>76</sub>O<sub>6</sub>I 863.4686, found 863.4688.

**(CN-Ligand)** : 1-(3',4',5'-Trioctyloxyphenyl)-3-(3''-cyano- 4''-

octyloxyphenyl)propane 1,3-dione

A red, viscous liquid in 33% yield.

$^1\text{H-NMR}$  (ppm,  $\text{CDCl}_3$ ) :

$\delta = 0.86$  (m, 12H,  $\text{CH}_3$  in OR group),  $\delta = 1.27-1.89$  (m, 48H,  $-(\text{CH}_2)_{24}$  in OR group),  $\delta = 4.00-4.16$  (m, 8H,  $-(\text{OCH}_2)_4$  in OR group),  $\delta = 6.61$  (s, 1H,  $\text{OHC}=\text{CH}$  for keto = enol form),  $\delta = 7.03$  (d, 1H, ArH),  $\delta = 7.15$  (s, 2H, ArH),  $\delta = 7.14$  (d, 1H, ArH),  $\delta = 8.16$  (s, 1H, ArH)

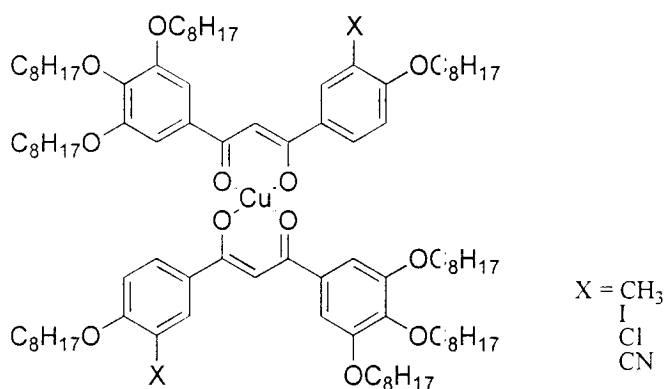
$^{13}\text{C-NMR}$  (ppm,  $\text{CDCl}_3$ ) :

$\delta = 13.95$  ( $\text{CH}_3$  in OR group),  $\delta = 22.55, 25.69, 26.02, 28.66, 29.06, 29.18, 29.27, 29.39, 30.27, 31.72, 31.78$  (C in OR group excluding  $-\text{OCH}_2-$ ),  $\delta = 69.25, 69.57, 73.45$  ( $-\text{OCH}_2-$ ),  $\delta = 91.76$  ( $\text{COCH}_2\text{CO}$ ),  $\delta = 105.78, 111.99, 132.83, 133.24$  (CH in Ar),  $\delta = 142.46, 153.04, 163.26$  (Aromatic C-OR),  $\delta = 102.22$  (Aromatic C-CN),  $\delta = 115.59$  (Ar-CN),  $\delta = 128.07, 129.70$  (Aromatic C- $\text{COCH}_2\text{CO}$ ),  $\delta = 182.33, 185.33$  (C=O)

$\text{IR}$  ( $\text{cm}^{-1}$ , Nujol) : 2958, 2923, 2858, 2233, 1607, 1589, 1465, 1379, 1338, 1282, 1199, 1118, 1013, 962, 793, 723

$\text{HRMS}$  (FAB) : Calcd for  $\text{MH}^+$   $\text{C}_{48}\text{H}_{76}\text{O}_6\text{N}$  762.5672, found 762.5671

(2) Preparation of copper(II) complexes :



The  $\beta$ -diketone,  $\text{Cu}(\text{OAc})_2$  and  $\text{K}_2\text{CO}_3$  were allowed to react in methanol under reflux to generate the corresponding copper(II) complex.

**( $\text{CH}_3\text{-Cu}$ )** : Bis[1-(3',4',5'-Trioctyloxyphenyl)-3-(3''-methyl-4''-octyloxyphenyl)propane 1,3-diketone] copper(II)

Green solid in 89% yield

$\text{IR}$ , ( $\text{cm}^{-1}$ , melt) : 2958, 2927, 2858, 1607, 1590, 1543, 1494, 1470, 1435, 1390, 1335, 1270, 1156, 1117, 777

$\text{MS}$  (FAB) : Calcd for  $\text{MH}^+$   $\text{C}_{96}\text{H}_{155}\text{CuO}_{12}$  1563.1, found 1563.8

$\text{Anal.}$  : Calcd for  $\text{C}_{96}\text{H}_{154}\text{CuO}_{12}$ : C, 73.73; H, 9.93; found:

**( $\text{Cl-Cu}$ )** : Bis[1-(3',4',5'-Trioctyloxyphenyl)-3-(3''-chloro-4''-octyloxyphenyl)propane 1,3-diketone] copper(II)

Green solid in 76% yield

IR ( $\text{cm}^{-1}$ , melt) : 2955, 2925, 2853, 1599, 1576, 1539, 1490, 1468, 1387, 1332, 1276, 1197, 1152, 1134, 1060, 980, 959, 773, 697

MS (FAB) : Calcd for  $\text{MH}^+$   $\text{C}_{94}\text{H}_{149}\text{Cl}_2\text{CuO}_{12}$  1603.0, found 1605.0

Anal. : Calcd for  $\text{C}_{94}\text{H}_{148}\text{Cl}_2\text{CuO}_{12}$ : C, 70.36; H, 9.30; found: C, 70.71; H, 9.35

**(I-Cu)** : Bis[1-(3',4',5'-Trioctyloxyphenyl)-3-(3''-iodo-4'-octyloxyphenyl)propane 1,3-diketonate] copper(II)

Green solid, in 90% yield

IR ( $\text{cm}^{-1}$ , melt) : 2958, 2928, 2858, 1593, 1569, 1538, 1484, 1467, 1436, 1390, 1335, 1265, 1198, 1117, 776

MS (FAB) : Calcd for  $\text{MH}^+$   $\text{C}_{94}\text{H}_{149}\text{CuI}_2\text{O}_{12}$  1786.9, found 1787.7

Anal. : Calcd for  $\text{C}_{94}\text{H}_{148}\text{CuI}_2\text{O}_{12}$ : C, 63.16; H, 8.35; found: C, 63.40; H, 8.48

**(CN-Cu)** : Bis[1-(3',4',5'-Trioctyloxyphenyl)-3-(3''-cyano-4'-octyloxyphenyl)propane 1,3-diketonate] copper(II)

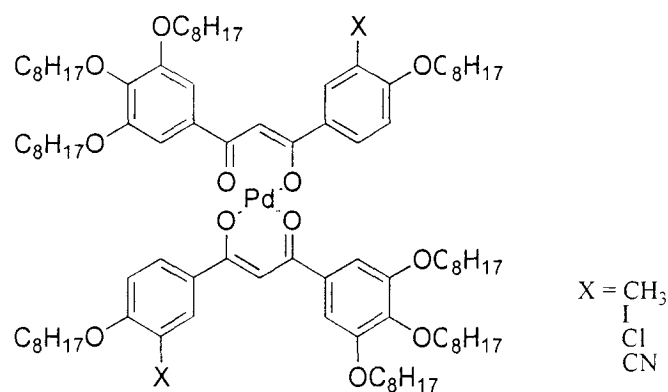
Green solid in 85% yield

IR ( $\text{cm}^{-1}$ , melt) : 2959, 2929, 2859, 2229, 1606, 1583, 1544, 1487, 1470, 1441, 1387, 1335, 1281, 1117, 776

MS (FAB) : Calcd for  $\text{MH}^+$   $\text{C}_{96}\text{H}_{149}\text{CuN}_2\text{O}_{12}$  1585.1, found 1586.1

Anal. : Calcd for  $\text{C}_{96}\text{H}_{148}\text{CuN}_2\text{O}_{12}$ : C, 72.71; H, 9.41; N, 1.77 found: C, 72.70; H, 9.51; N, 1.59

(3) Preparation of palladium (II) complexes :



The  $\beta$ -diketone,  $\text{Pd}(\text{OAc})_2$  and  $\text{K}_2\text{CO}_3$  were allowed to react in chloroform under reflux to generate the corresponding copper(II) complex.

**(CH<sub>3</sub>-Pd)** : Bis[1-(3',4',5'-Trioctyloxyphenyl)-3-(3''-methyl-4'-octyloxyphenyl)propane 1,3-diketonate] palladium(II)

Yellow solid in 79% yield

IR ( $\text{cm}^{-1}$ , melt) : 2955, 2925, 2855, 1610, 1591, 1534, 1493, 1430, 1467, 1383, 1334, 1268, 1131, 1115, 771

MS (FAB) : Calcd for  $\text{MH}^+$   $\text{C}_{96}\text{H}_{155}\text{O}_{12}\text{Pd}$  1606.1, found 1606.1



Anal. : Calcd for  $C_{96}H_{154}O_{12}Pd$ : C, 71.77; H, 9.66; found: C, 71.70; H, 9.53

**(Cl-Pd)** : Bis[1-(3',4',5'-Trioctyloxyphenyl)-3-(3''-chloro-4''-octyloxyphenyl)propane 1,3-diketonate] palladium(II)

Yellow solid in 82% yield

IR ( $cm^{-1}$ , melt) : 2955, 2926, 2856, 1598, 1575, 1532, 1489, 1467, 1431, 1378, 1334, 1273, 1204, 1119, 1062, 770

MS (FAB) : Calcd for  $MH^+ C_{94}H_{149}Cl_2O_{12}Pd$  1645.9, found 1645.9

Anal. : Calcd for  $C_{94}H_{148}Cl_2O_{12}Pd$ : C, 68.53; H, 9.05; found: C, 68.70; H, 9.19

**(I-Pd)** : Bis[1-(3',4',5'-Trioctyloxyphenyl)-3-(3''-iodo-4''-octyloxyphenyl)propane 1,3-diketonate] palladium(II)

Deep yellow solid in 84% yield

IR ( $cm^{-1}$ , melt) : 2959, 2928, 2858, 1594, 1566, 1531, 1504, 1485, 1469, 1433, 1380, 1337, 1263, 1202, 1118, 773

MS (FAB) : Calcd for  $MH^+ C_{94}H_{149}I_2O_{12}Pd$  1829.8, found 1828.6

Anal. : Calcd for  $C_{94}H_{148}I_2O_{12}Pd$ : C, 61.68; H, 8.15; found:

**(CN-Pd)** : Bis[1-(3',4',5'-Trioctyloxyphenyl)-3-(3''-cyano-4''-octyloxyphenyl)propane 1,3-diketonate] palladium(II)

Orange solid in 86% yield

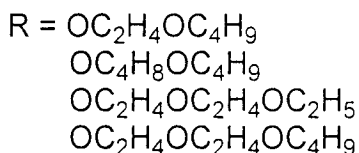
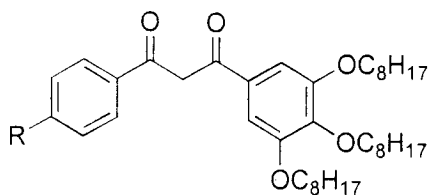
IR ( $cm^{-1}$ , melt) : 2959, 2929, 2859, 2229, 1606, 1582, 1539, 1492, 1469, 1434, 1381, 1335, 1282, 1204, 1117, 771

MS (FAB) : Calcd for  $MH^+ C_{96}H_{149}N_2O_{12}Pd$  1628.0, found 1628.0

Anal. : Calcd for  $C_{96}H_{148}N_2O_{12}Pd$ : C, 70.80; H, 9.16; N, 1.72 found: C, 70.78; H, 9.26; N, 1.27

### 3. Synthesis of 4''-alkoxy $\beta$ -diketonate ligands and preparation of complexed

#### (1) Synthesis of ligands



From substituted acetophenone, 3,4,5-trialkoxybenzoate and sodium hydride (NaH) in tetrahydrofuran solution under reflux the following ligands were made:

1-(3',4',5'-Trioctyloxyphenyl)-3-{4''-[(oxy)ethyl]oxy}butyl]-phenyl}-propane-1,3-dione

$^1H$ -NMR (ppm,  $CDCl_3$ ):  $\delta$  = 0.90 (m, 12H,  $-(CH_3)_4$  in OR group),  $\delta$  = 1.27-1.81 (m,

40H,  $-(\text{CH}_2)_{20}$  in OR group),  $\delta = 3.53$  (t, 2H,  $\text{CH}_2\text{-O-CH}_2$ ),  $\delta = 3.79$  (t, 2H,  $\text{CH}_2\text{OCH}_2$ ),  $\delta = 4.01\text{-}4.20$  (m, 8H,  $-(\text{OCH}_2)_4$ ),  $\delta = 6.66$  (s, 1H,  $\text{OHC=CH}$  for keto = enol form),  $\delta = 6.98$  (d,  $J = 8.88$  Hz, 2H, ArH),  $\delta = 7.16$  (s, 2H, ArH),  $\delta = 7.93$  (d,  $J = 8.84$  Hz, 2H, ArH)

$^{13}\text{C-NMR}$  (ppm,  $\text{CDCl}_3$ ):  $\delta = 13.87, 14.06, 19.24, 22.65, 26.09, 29.27, 29.35, 29.49, 30.32, 31.66, 31.80, 31.88, 67.66, 68.93, 69.41, 71.45, 73.58, 91.99, 105.97, 114.57, 128.09, 129.07, 130.61, 142.25, 153.11, 162.42, 184.61, 185.07$

$\text{IR}$  ( $\text{cm}^{-1}$ , Nujol): 2928, 2861, 1464, 1379, 723

Elemental Anal.: Calcd: C, 74.55; H, 10.01. Found: C, 74.54; H, 10.12.

1-(3',4',5'-Trioctyloxyphenyl)-3-{4''-[[{(oxy) butyl]oxy}butyl]yl]-phenyl}-propane-1,3-dione

$^1\text{H-NMR}$  (ppm,  $\text{CDCl}_3$ ):  $\delta = 0.90$  (m, 12H,  $-(\text{CH}_3)_4$  in OR group),  $\delta = 1.27\text{-}1.85$  (m, 44H,  $-(\text{CH}_2)_{22}$  in OR group),  $\delta = 3.38$  (m, 4H,  $\text{CH}_2\text{OCH}_2$ ),  $\delta = 3.97\text{-}4.08$  (m, 8H,  $-(\text{OCH}_2)_4$ ),  $\delta = 6.66$  (s, 1H,  $\text{OHC=CH}$  for keto = enol form),  $\delta = 6.94$  (d,  $J = 9.05$  Hz, 2H, ArH),  $\delta = 7.15$  (s, 2H, ArH),  $\delta = 7.92$  (d,  $J = 9.02$  Hz, 2H, ArH)

$^{13}\text{C-NMR}$  (ppm,  $\text{CDCl}_3$ ):  $\delta = 13.38, 14.03, 19.35, 22.62, 26.03, 26.07, 26.24, 29.25, 29.32, 29.36, 29.48, 30.31, 31.79, 31.84, 67.95, 69.18, 69.37, 70.24, 70.68, 73.53, 91.88, 105.94, 107.7, 114.30, 114.38, 127.76, 129.08, 130.59, 131.32, 142.20, 152.89, 153.07, 162.65, 184.66, 184.93$

$\text{IR}$  ( $\text{cm}^{-1}$ , Nujol): 2928, 2958, 2858, 1463, 1379, 723

Elemental Anal.: Calcd: C, 74.96; H, 10.17. Found:

1-(3',4',5'-Trioctyloxyphenyl)-3-[4''-[[[[(oxy)ethyl]oxy]ethyl]oxy]ethyl]yl]phenyl]-propane-1,3-dione

$^1\text{H-NMR}$  (ppm,  $\text{CDCl}_3$ ):

$\delta = 0.87$  (m, 12H,  $-(\text{CH}_3)_4$  in OR group),  $\delta = 1.16\text{-}1.85$  (m, 36H,  $-(\text{CH}_2)_{18}$  in OR group),  $\delta = 3.47\text{-}4.20$  (m, 16H,  $-(\text{OCH}_2)_8$ ),  $\delta = 6.66$  (s, 1H,  $\text{OHC=CH}$  for keto = enol form),  $\delta = 6.98$  (d,  $J = 8.95$  Hz, 2H, ArH),  $\delta = 7.15$  (s, 2H, ArH),  $\delta = 7.93$  (d,  $J = 8.86$  Hz, 2H, ArH)

$^{13}\text{C-NMR}$  (ppm,  $\text{CDCl}_3$ ):  $\delta = 14.06, 15.11, 22.64, 26.09, 29.25, 29.34, 29.48, 30.31, 31.79, 66.69, 67.61, 69.39, 69.54, 70.97, 73.57, 91.98, 105.96, 114.54, 128.12, 129.08, 130.54, 142.25, 153.10, 162.34, 184.58, 185.07$

$\text{IR}$  ( $\text{cm}^{-1}$ , Nujol): 2923, 2859, 1464, 1379, 723

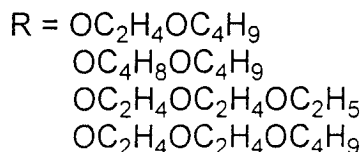
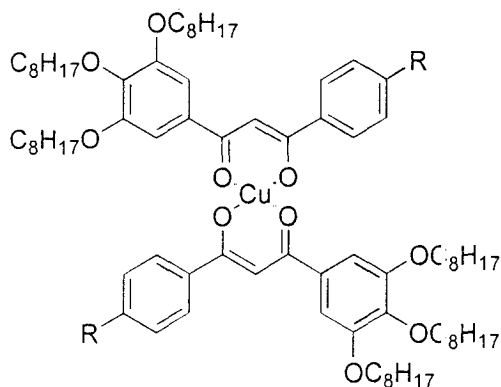
Elemental Anal.: Calcd: C, 72.93; H, 9.79. Found: C, 73.09; H, 9.61

1-(3',4',5'-Trioctyloxyphenyl)-3-[4''-[[[[(oxy)ethyl]oxy]ethyl]oxy]butyl]yl]phenyl]-propane-1,3-dione

$^1\text{H-NMR}$  (ppm,  $\text{CDCl}_3$ ):  $\delta = 0.83\text{-}0.93$  (m, 12H,  $-(\text{CH}_3)_4$  in OR group),  $\delta = 1.20\text{-}1.85$  (m, 40H,  $-(\text{CH}_2)_{20}$  in OR group),  $\delta = 3.42\text{-}4.22$  (m, 16H,  $-(\text{OCH}_2)_8$ ),  $\delta = 6.66$  (s, 1H,  $\text{OHC=CH}$  for keto = enol form),  $\delta = 6.98$  (d,  $J = 8.90$  Hz, 2H, ArH),  $\delta = 7.16$  (s, 2H, ArH),  $\delta = 7.93$  (d,  $J = 8.85$  Hz, 2H, ArH)

$^{13}\text{C-NMR}$  (ppm,  $\text{CDCl}_3$ ):  $\delta = 13.89, 14.06, 19.25, 22.64, 26.08, 29.27, 29.34, 29.49, 30.31, 31.67, 31.80, 67.63, 69.41, 69.55, 70.09, 70.94, 71.27, 73.57, 76.36, 76.99, 77.62, 91.98, 105.97, 114.55, 128.12, 129.09, 130.61, 142.25, 153.11, 162.35, 184.58, 185.07$   
 $\text{IR}$  ( $\text{cm}^{-1}$ , Nujol): 2927, 2957, 2858, 1464, 1379, 723  
Elemental Anal.: Calcd: C, 73.40; H, 9.96. Found: C, 73.19; H, 9.44

## (2) Preparation of Copper(II) complexes :



The  $\beta$ -diketone,  $\text{Cu}(\text{OAc})_2$  and  $\text{K}_2\text{CO}_3$  were allowed to react in methanol under reflux to generate the corresponding copper(II) complex.

Bis[1-(3',4',5'-trioctyloxyphenyl)-3-{4''-[({(oxy)ethyl}oxy)butyl]yl]phenyl]-propane-1,3-dione] copper(II)

$\text{IR}$  ( $\text{cm}^{-1}$ , KBr): 2926, 2857, 1539, 1493, 1334, 1255, 1117, 777  
 Elemental Anal.: Calcd: C, 71.51; H, 9.47. Found: C, 70.62; H, 8.92

Bis[1-(3',4',5'-trioctyloxyphenyl)-3-{4''-[({(oxy)butyl}oxy)butyl]yl]phenyl}-propane-1,3-dione] copper(II)

$\text{IR}$  ( $\text{cm}^{-1}$ , KBr): 2954, 2925, 2871, 2854, 1537, 1492, 1334, 1247, 1132, 1116, 775  
 Elemental Anal. : Calcd: C, 72.02; H, 9.64. Found: C, 71.39; H, 9.01

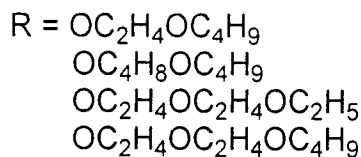
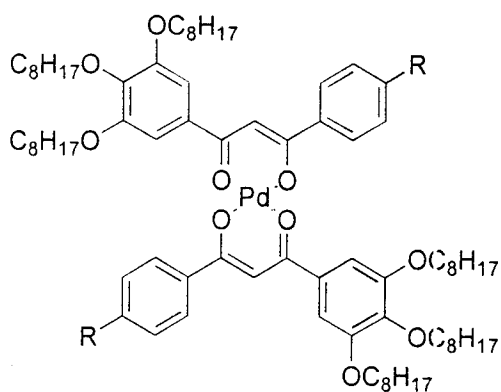
Bis{1-(3',4',5'-trioctyloxyphenyl)-3-[4''-(([({(oxy)ethyl}oxy)ethyl]oxy)ethyl)yl]phenyl}-propane-1,3-dione} copper(II)

$\text{IR cm}^{-1}$ (KBr):2925,2926,2872,2856,1539,1492,1437,1390,1254,1125,781  
 Elemental Anal. Calcd: C,70.03;H,9.27.Found:C,69.96;H,8.94

Bis{1-(3',4',5'-trioctyloxyphenyl)-3-[4''-(([({(oxy)ethyl}oxy)ethyl]oxy)butyl)yl]-phenyl]-propane-1,3-dione} copper(II)

$\text{IR}$  ( $\text{cm}^{-1}$ , KBr): 2925, 2928, 2854, 1538, 1492, 1444, 1335, 1253, 1133, 1117, 775

## (3) Preparation of palladium(II) complexes



The  $\beta$ -diketone,  $\text{Pd}(\text{OAc})_2$  and  $\text{K}_2\text{CO}_3$  were allowed to react in chloroform under reflux to generate the corresponding copper(II) complex.

Bis[1-(3',4',5'-trioctyloxyphenyl)-3-{4''-[[{(oxy)ethyl]oxy}butyl]yl phenyl]-propane-1,3-dione] palladium(II)

IR ( $\text{cm}^{-1}$ , KBr): 2926, 2857, 1531, 1491, 1334, 1254, 1117, 773

Elemental Anal : Calcd: C, 69.54; H, 9.21. Found: C, 69.89; H, 9.36

Bis[1-(3',4',5'-trioctyloxyphenyl)-3-{4''-[[{(oxy)butyl]oxy}butyl]yl]Phenyl]-propane-1,3-dione] palladium(II)

IR ( $\text{cm}^{-1}$ , KBr): 2952, 2926, 2871, 2856, 1530, 1491, 1469, 1334, 1251, 1116, 773

Elemental Anal : Calcd: C, 70.10; H, 9.39. Found: C, 69.88; H, 9.35

Bis{1-(3',4',5'-trioctyloxyphenyl)-3-[4''-[[[[(oxy)ethyl]oxy]ethyl]oxy]ethyl]yl]phenyl]-propane-1,3-dione} palladium(II)

IR ( $\text{cm}^{-1}$ , KBr): 2954, 2926, 2873, 2857, 1531, 1491, 1335, 1252, 1118, 773

Elemental Anal : Calcd: C, 68.14; H, 9.02. Found: C, 68.09; H, 8.72

Bis{1-(3',4',5'-trioctyloxyphenyl)-3-[4''-[[[[(oxy)ethyl]oxy]ethyl]oxy]butyl]yl]phenyl]-propane-1,3-dione} palladium(II)

IR ( $\text{cm}^{-1}$ , KBr): 2956, 2928, 2871, 2855, 1530, 1492, 1469, 1388, 1335, 1252, 1133, 1122, 771

Other studies are in progress.