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Synthesis and mesomorphic properties of γ-substituted β-diketones and their dicarbonylrhodium(I) complexes

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Abstract

Five series of 3-($C_{10}H_{21}O$–Ph–X–Ph–Y–) substituted pentane-2,4-diones and their dicarbonylrhodium(I) complexes, namely, series 1: X = –CH=CHCOO– and Y = –COO–, series 2: X = –CH=CHCOO– and Y = –CH=CHCOO–, series 3: X = –COO– and Y = –CH=CHCOO–, series 4: X = –CH_2O– and Y = –COO–, series 5: X = –N=N– and Y = –COO–, have been synthesized, their mesogenic properties have been investigated using a Nikon polarizing microscope and DSC. It is found the β-diketones **1a**–**3a**, **5a** and the complexes **1b**–**3b** exhibit liquid crystal behaviors. The effect of the bridging groups of X and Y on the mesogenic properties of the ligands and the complexes has been explored.

Keywords: Liquid crystal; β-Diketone; Organometallic complexes

1. Introduction

In recent years, there has been a continuing interest in the synthesis of various β-diketones because they can be widely used as organic ligands in mesogenic coordination complexes of most transition metal ions [1–6]. Although a large number of β-diketones have been reported to date, only a few examples of mesogenic 3-substituted pentane-2,4-dione have been published [7,8]. To the best of our knowledge, the relationship between the molecular structure of the β-diketones and its mesogenic properties has not been explored in detail yet. So far, the metal ion of β-diketone complexes is most situated at the center of the molecules, such molecules have always central symmetry, which will be disadvantageous to further enhancement of electro-optic response. Our results [9,10]and recent reports [11,12]show that the β-diketone complexes with terminal metal ion have not only good conjugation structure, but also have great dipole moments, both factors are beneficial to improve the mesogenic properties. We are endeavoring to understand the relationship between the molecular structures and the mesogenic properties, herein, we report the synthesis of five series of new β-diketones and their corresponding complexes based on dicarbonylrhodium(I) as the terminal group (Chart 1), the relationship between the molecular structure and the mesogenic properties has also been explored.

2. Results and discussion

2.1. Synthesis and characterization

Compound 2,4-dioxo-3-pentyl 4-hydroxybenzoate **7** is a key intermediate in the synthesis of γ-substituted β-diketone. The synthesis of **7** had been reported by Serrano and co-workers which is outlined in Scheme 1 [8].

The three-step synthesis of **7** by Serrano was undertaken using $BrCH_2Ph$ as the protecting reagent and the expensive Pd/C catalyst as the deprotecting reagent, and the phase transfer catalyst are used in the reaction. Generally speaking, the procedure above is complicated and the total yield is about 40%.

A practical and facile method for the synthesis of **7** has been found, which is outlined in Scheme 2. The

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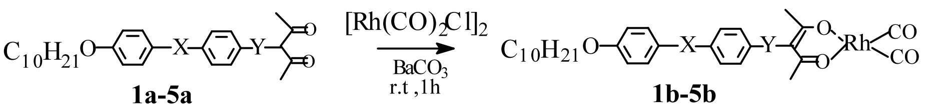
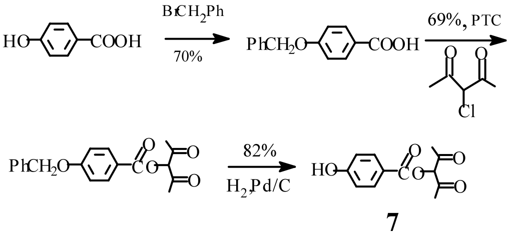
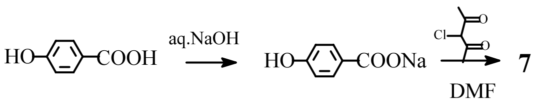


Chart 1.



Scheme 1. The synthesis of **7** by Serrano and co-workers.



Scheme 2. A practical and facile synthesis of **7**.

synthesis of **7** was undertaken using the available 3-chloropentane-2,4-dione and the sodium 4-hydroxybenzoate solid in dry DMF at 50 °C overnight, the sodium 4-hydroxybenzoate was obtained nearly stiochio-metrically by the reaction of 4-hydroxybenzoic acid with the aqueous solution of NaOH. It’s unnecessary to use any phase transfer catalyst and protecting reagent in Scheme 2, all the reactions are operated simply and in mild conditions, the total yield is about 80% which is nearly two times of Serrano’s method.

The compound 2,4-dioxo-3-pentyl 4-hydroxycinnamate **8** is another key intermediate in the synthesis of γ-substituted β-diketone, it was obtained in good yield using the similar procedure to prepare the compound **7**. The route to synthesize **8** is outlined in Scheme 3. The compound 4-hydroxycinnamic acid was obtained according to the literature reported previously [13].

The synthesis of **1a**, **2a** and **3a** is outlined in Scheme 4. This method seemed to be the most facile for preparation of the compounds with the general structures **1a**, **2a** and **3a**. Compounds **9** [14], **10** [15,16] were refluxed with $SOCl_2$ to give the compounds **11** and **12**, respectively, which were then reacted with **7** or **8** to obtain **1a**, **2a** and **3a** in excellent yield. The overall reaction sequence was carried out simply without chromatographic purification.

The synthesis of **4a** is outlined in Scheme 5, which was carried out by the reaction of the commercially available methyl 4-hydroxybenzoate with the compound **13** [17] to give the compound **14** smoothly. The β-diketone **4a** was obtained by the reaction of 3-chloropentane-2,4-dione with the compound **14** according to the similar procedure reported before [18].

The β-diketone **5a** was synthesized in a typical method, which is outlined in Scheme 6.

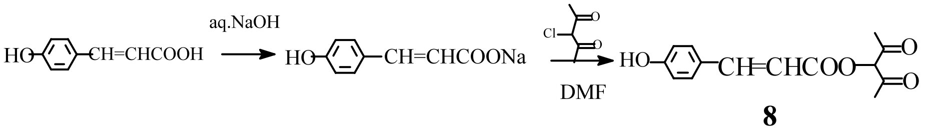
The structures of the compounds were confirmed by the elemental analyses, MS, ^{1}H-NMR, infrared (IR) and UV–vis spectroscopies.

The IR spectra of the ligands show a strong stretching vibration frequency at ca. 1730 cm^{-1}, which is assigned to the $\nu_{C=O}$ and ν_{COO}. In contrast, the stretching vibration frequency at ca. 1730 cm^{-1} in the IR spectra of the complexes becomes weaker than that of the corresponding free ligands, which implies the two carbonyl groups have chelated with the metal ion [9]. The IR spectra of the complexes appear absorption at ca. 2080 and 2010 cm^{-1}, which are the characteristic of the carbon monoxide (CO) stretching region [19].

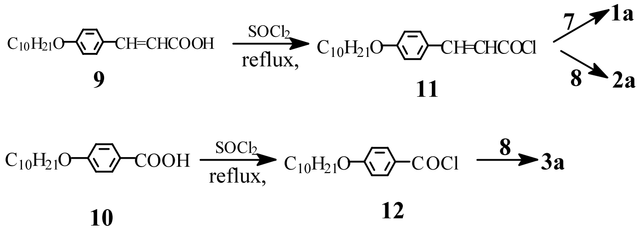
From the ^{1}H-NMR data of the compounds **1a**–**5a**, it is found that **1a**–**3a** and **5a** exist in both of keto form and enol form in the solution of $CDCl_3$ (Chart 2). The ^{1}H-NMR spectra for **1a**–**3a** and **5a** show a signal (δ) at ca. 14.50 ppm due to the enolic proton, a signal at 2.10 ppm for the CH_3 proton in the enol form. While, the signals at ca. 5.71 and 2.37 ppm are assigned to the CH and CH_3 protons in the keto form, respectively.

The UV–vis data of the ligands **1a**–**5a** and the complexes **1b**–**5b** are summarized in Table 1.

The UV–vis data in Table 1 show that the λ_{max} of **1a**–**5a** and **1b**–**5b** decrease according to the order: **4a**,**4b** > **2a**,**2b** > **1a**,**1b** > **3a**,**3b** > **4a**,**4b**. This may be explained by the structures of the compounds. As to the compounds **1a**–**3a**,**5a** and **1b**–**3b**,**5b**, the bridging groups between the two benzene rings are $-CH{=}CHCO_2-$, $-CO_2-$and $-N{=}N-$, respectively, while the compounds **4a**,**4b** have the $-CH_2O-$ as the bridging group. $-CH{=}CHCO_2-$, $-CO_2-$ and $-N{=}N-$ are all unsaturated groups which can be conjugated with the benzene rings and make a long conjugated structure. In contrast, the $-CH_2O-$ is a saturated group which is disadvantageous to form long conjugated system, so the λ_{max} of **4a**,**4b** are the shortest



Scheme 3. Synthesis of **8**.



Scheme 4. Synthesis of **1a**, **2a**, **3a**.

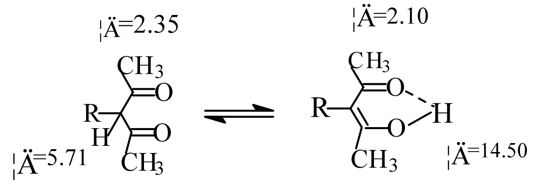
among all the compounds. On basis of the λ_{max} of the compounds **1a**–**3a**,**5a** and **1b**–**3b**,**5b**, we can find that the conjugation of the bridging groups X increase according to the order $-CO_2- < -CH{=}CHCO_2- < -N{=}N-$. By comparison the λ_{max} of the ligands and the corresponding complexes, it is found that the λ_{max} of the complexes are larger than that of the corresponding ligands. The formation of the six-membered metalacycle extends the conjugated system because of its aromaticity, which may explain the change of the λ_{max} between the ligands and the complexes.

2.2. *Mesomorphism*

The textures of the mesophases were studied with a Nikon polarizing microscope equipped with a hot stage. All mesophases had been identified according to the textures observed by optical microscopy [20,21]. The β-diketones **1a** and **3a** both exhibit one monotropic phase (N), and **2a** display two monotropic phases (N and Sc), while **5a** exhibit two enantiotropic phases (N and Sc); The complexes **1b**,**3b** exhibit one enantiotropic phase (Sc), and **2b** displays one enantiotropic smectic A phase. The typical texture of the ligands and the complexes are shown in Figs. 1–3.

The transition temperatures were measured by differential scanning calorimetry using DSC-7 instrument operated at a scanning rate of 5 °C min^{-1} on heating and cooling. The optical, thermal, and thermodynamic data of the new β-diketones **1a**–**5a** are given in Table 2.

From Table 2, it is found the following results: (i) the β-diketones **1a**,**2a**,**3a** and **5a** are all mesogens while **4a** does not display mesophism; (ii) the β-diketone **5a** exhibits two enantiotropic phases (N and Sc), the temperature range of mesophase is from 78.5 to 184.5 °C, which is the widest among the compounds **1a**,**2a**,**3a** and **5a**; (iii) the β-diketone **2a** displays two monotropic phases (N and Sc) and the mesomorphic temperature range is about 40 °C,while **1a** and **3a** both have one monotropic phase (N) and a narrow meso-

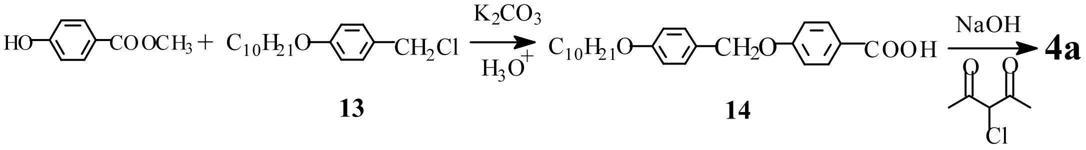


1a-3a,5a

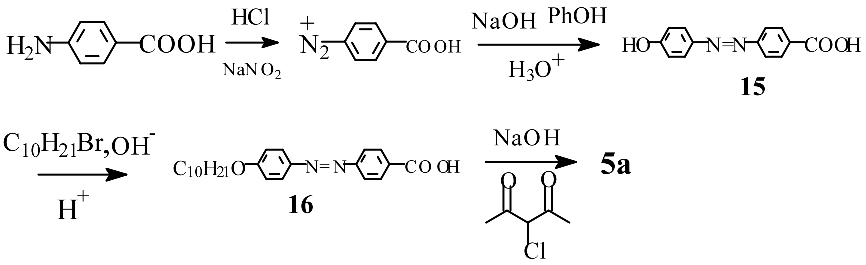
Chart 2.

Table 1
The UV–vis data of **1a**–**5a** and **1b**–**5b**

Compound	λ_{max} (nm)	ε_{max} (dm^3 mol^{-1} cm^{-1}) ($CHCl_3$)	log ε_{max}
1a	320.2	28 183	4.45
2a	321.6	41 687	4.62
3a	287.4	26 915	4.43
4a	263.6	20 417	4.31
5a	361.5	29 054	4.46
1b	321.0	31 623	4.50
2b	323.0	47 863	4.68
3b	288.0	30 651	4.48
4b	267.5	28 184	4.45
5b	363.2	31 248	4.49



Scheme 5. Synthesis of **4a**.



Scheme 6. Synthesis of **5a**.

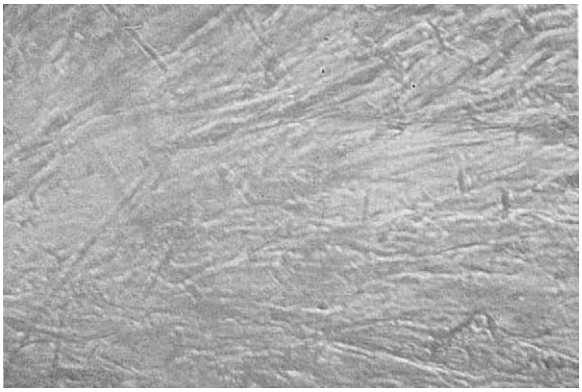


Fig. 1. Texture of the ligand **1a** under crossed polarizers, 68 °C, upon cooling run, × 250 N phase.

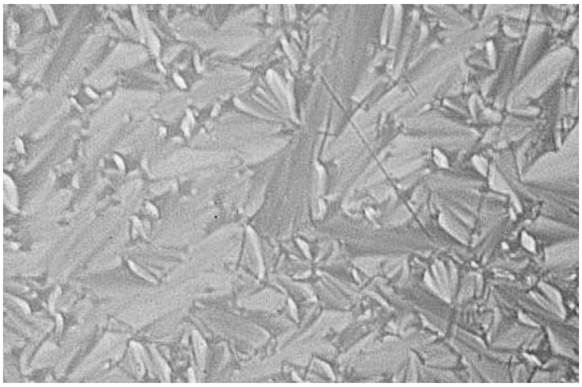


Fig. 2. Texture of the complex **2b** under crossed polarizers, 120 °C, upon cooling, × 250 Sc phase.

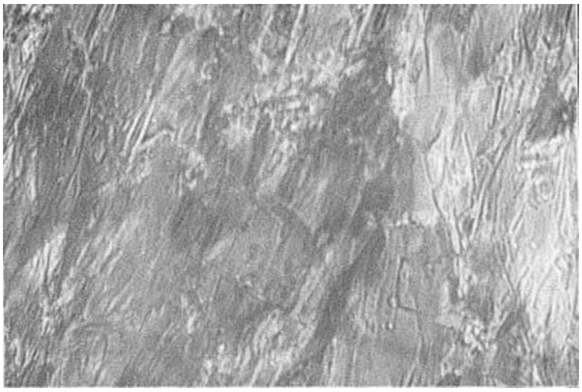


Fig. 3. Texture of the complex **3b** under crossed polarizers, 124 °C, upon heating, × 250 N phase.

morphic temperature range about 20 °C. The mesomorphic behaviors observed can be explained using geometrical and electronic factors associated with the molecules. From the structures of the compounds **1a**–**4a** and **5a**, we can see the bridging group X is CH_2O, the corresponding compounds **4a** does not display liquid crystal behaviors. This is because the bridging group CH_2O disrupts the electronic conjugation and cannot form enough mesogenic core, which is the basic factor to the formation of mesomorphic phases. In contrast, when the bridging group is an azo, an ester or an acrylic ester, the aromatic conjugation can be extended to the β-diketone, and this fact favors molecular polarizability, thus increasing molecular interactions and consequently promoting liquid crystal behavior. The conjugation of the bridging group increases according to the order $-CO_2- < -CH{=}CHCO_2- < -N{=}N-$, which may explain the different liquid crystal behaviors of the β-diketones **1a**,**2a**,**3a** and **5a**. The conjugation of the bridging groups may increase the molecular rigidity and planarity, the intermolecular interactions and the ordered arrangement of molecules increase consequently. All of these factors are beneficial to form the mesomorphism and increase the stability of the thermotropic mesogenic phase. Owing to the most conjugation of the azo group, **5a** has the best mesomorphism than that of the **1a**,**2a** and **3a**. By comparison of the mesomorphic properties of **1a** with that of **2a** and **3a**, we can see that the compound **2a** has not only wider mesogenic temperature range but also more mesogenic phases than **2a** and **3a**. The bridging groups X and Y in compound **1a** are two acrylic ester groups, which are more effective to form conjugation structure than the ester group; On the other hand, the length-to-breadth ratio of **2a** is greater than that of **1a** or **3a**. Both of the factors favor the parallel molecular organization and form mesomorphism.

Table 2
Optical, thermal and thermodynamic data of the γ-substituted β-diketones

Compound	Transition	Temperature (°C)	ΔH (kJ mol^{-1})
1a	C–I	108.62	43.66
	I–N	73.84	−2.49
	N–C	54.92	−0.078
2a	C–I	126.8	47.48
	I–N	106.8	−0.53
	N–Sc	98.7	−0.45
	Sc–C	68.9	−4.11
3a	C–I	66.52	18.12
	I–N	52.39	−0.37
	N–C	48.36	−1.22
4a	C–I	62.30	42.08
5a	C–N	78.5	46.23
	N–Sc	138.7	−0.74
	Sc–I	184.5	−0.61

The optical, thermal and thermodynamic data of the organometallic complexes are given in Table 3.

If the mesomorphism of the organometallic complexes are compared with that of the corresponding organic ligands, we find that the organic ligands **1a**,**2a**,**3a** all display monotropic phases, whereas the complexes **1b**–**3b** all possess enantiotropic phases. Two factors may be attributed to this improvement of mesomorphic behavior: (i) the chelating ring of the β-diketone complexes is not only six-membered conjugation structure but also planar because of its aromaticity, which may enhance the rigidity and extend the con-

Table 3
The optical, thermal and thermodynamic data of the organometallic complexes

Compound	Transition	Temperature (°C)	ΔH (kJ mol^{-1})
1b	C–N	101.5	18.83
	N–I	142.4	1.71
2b	C–S_A	118.40	19.00
	S_A–I	128.49	3.25
3b	C–N	114.6	21.43
	N–I	130.2	2.12
4b	C–I	111.2	29.08
5b	–	168	–

jugated system of the complexes; and (ii) the terminal carbon monoxides in the complexes are strong ligands which can be easily coordinated with the metal rhodium(I) by the d–π and π–π* interaction. Both interactions tend to reduce the strength of the C≡O bond and extend the conjugation of the mesogenic core, which can be confirmed experimentally by comparing the vibrational spectra of free and coordinated CO. The free molecule has a stretching frequency $\nu_{CO} = 2143$ cm^{-1} [22], whereas the terminal groups in the complexes **1b**–**5b** have ν_{CO} at 2080 and 2010 cm^{-1}, which implies that the CO ligand accepts π-back donation from metal ion and may give rise to a large dipole moment of the complexes. Both of the factors lead to the complexes have not only good conjugation structure, but also great dipole moments and facilitate the formation of liquid crystal phases.

We expect the complex **5b** has better mesomorphism than **5a**, unfortunately, when **5b** was heated above 168 °C before the melting point, it decomposed partly and didnot appear mesomorphism. The reason that the complex **4b** did not show mesogenic phase is probably due to the bridging group –CH_2O–, which disrupts the conjugation of the molecule.

3. Conclusion

General methods for the syntheses of five series of new γ-substituted β-diketones and their corresponding dicarbonylrhodium(I) complex have been reported. The mesogenic properties of the ligands and the complexes have also explored. The results shown that the bridging group between the two benzene rings affects the liquid crystal properties of the ligands and the complexes greatly. The formation of the six-membered metalacycles may extend the conjugated system of the complexes, and the terminal CO ligands accepts π-back donation from Rh(I) which may give rise to a large dipole moment of the complexes. Both of the factors are beneficial to form the mesomorphism.

4. Experimental

4.1. Techniques

IR and UV–vis spectroscopies were recorded on, respectively a NICOLET FT-MX-IE spectrometer in KBr pellets and UV-2401PC SHIMADZU. The ^{1}H-NMR spectra were carried on 300 MHz Brucker AC-P300 spectrometer in $CDCl_3$ solution, with Me_4Si as internal standard, ^{1}H-NMR peak frequencies are quoted in ppm and coupling constants in Hz. Elemental analysis was performed with a CARLO ERBA-1106 microanalyzer. The Mass spectra were taken on a Finnigan MAT4510 spectrometer (70 eV, direct insertion probe).

The optical observations were made with a ORTH-LUX-II POLBK polarizing optical microscope with a hot stage and TDA temperature controller. The transition temperatures and enthalpies were measured on a Perkin–Elmer DSC-7 differential scanning calorimeter with a heating and cooling rate of 5.0 °C min^{-1}. The apparatus was calibrated with indium (156.6 °C, 3.3 kJ mol^{-1}) and tin (232.1 °C, 7.2 kJ mol^{-1}).

4.2. Synthesis

4.2.1. Synthesis of 2,4-dioxo-3-pentyl 4-hydroxybenzoate (7) (general procedure for *8*)

A mixture of 3-chloropentane-2,4-dione (6.73 g, 0.05 mol) and sodium 4-hydrobenzoate (8 g, 0.05 mol) in anhydrous DMF (60 ml) was stirred at 50 °C for 24 h. After cooling at room temperature, 200 ml of water was added and the mixture was extracted twice with $CHCl_3$. The combined extracts were dried over sodium sulfate. The solvent was evaporated under reduced pressure, the remainder was chromatographed on silica gel (EtOAc–petrodeum ether 1:1) and further purified by recrystallization in benzene to obtain a white solid. Yield: 79.7%; m.p. 109.5 °C; ν_{max} (KBr)/cm^{-1} 3500–3100, 1724, 1613, 1571, 1254, 1169; δ_H ($CDCl_3$) 13.90, 5.70 (2 × s, 1H), 6.93–7.98 (m, 4H, ArH), 2.16, 1.97 (2 × s, 6H, 2 × CH_3); m/z (%): 236 (M^+, 4.78), 147 (100); Anal. Found: C, 60.95; H, 5.11; Calc. for $C_{12}H_{12}O_5$: C, 61.20; H, 5.08%.

4.2.2. Data for 2,4-dioxo-3-pentyl 4-hydrocinnate (*8*)

Yield: 76.4%; white powder; ν_{max} (KBr)/cm^{-1} 3366, 1716, 1631, 1605, 1580, 1515, 1266, 1204, 1149, 985; δ_H ($CDCl_3$) 14.45, 5.64 (1H, 2 × s, CH), 7.70, 6.35 (2H, 2 × d, J 16, –CH=CH–), 7.40, 6.85 (4H, 2 × d, J 8.0, ArH), 2.36, 2.05 (2 × s, 6H, 2 × CH_3); m/z (%): 262 (M^+, 2.52), 147 (100); Anal. Found: C, 63.88; H, 5.31. Calc. for $C_{14}H_{14}O_5$: C, 64.12; H, 5.34%.

4.2.3. Synthesis of 4-[[4-(n-decyloxy)]oxy]benzoic acid (**14**)

To a suspension of the compound **13** (5.65 g, 0.02 mol) in 50 ml of EtOH was added methyl 4-hydroxybenzoate (3.04 g, 0.02 mol) and K_2CO_3 (5.52 g, 0.04 mol) under stirring. The mixture was refluxed for 12 h. After cooling to room temperature, the mixture was neutralized to pH 7 with 2 M HCl. The precipitate was filtered and washed twice with EtOH. The product was purified by recrystallization in EtOH to give a white solid. Yield: 62%; white powder; ν_{max} (KBr)/cm^{-1} 2920, 2851, 3500–2500, 1681, 1608, 1515, 1249; δ_H ($CDCl_3$) 8.06, 7.05 (4H, 2 × d, *J* 9.3, ArH), 7.35, 6.89 (4H, 2 × d, *J* 8, ArH), 5.03 (2H, s, $ArCH_2O$), 3.95 (2H, t, *J* 6.6, RCH_2OAr), 1.85 (2H, m, CH_2), 1.35 (14H, m, 7 × CH_2), 0.87 (3H, t, *J* 6.0, CH_3). Anal. Found: C, 74.89; H, 8.56. Calc. for $C_{24}H_{32}O_4$ C, 75.00; H, 8.33%.

4.2.4. Synthesis of 4-(4-hydroxyphenylazo)benzoic acid (**15**)

In a typical preparation, 20 ml of H_2O containing HCl (9 ml, 12 M, 0.11 mol) was added to the compound 4-aminobenzoic acid (10 g, 0.073 mol). To the resulting solution, stirred and cooled to 0 °C, an aqueous $NaNO_2$ (5.1 g, 0.074 mol) solution (20 ml) was added dropwise, and the so-formed diazonium chloride was consecutively adjusted to pH 8 with an aqueous solution of K_2CO_3 and then coupled with phenol (6.9 g, 0.73 mol), dissolved in 40 ml of aqueous NaOH (2.9 g, 0.073 mol) solution. The reaction mixture was stirred for 30 min at 0 °C and allowed to warm slowly to room temperature. The mixture was adjusted to pH 6 with an aqueous HCl solution and the red precipitate was filtered, washed several times with water and recrystallized in the EtOH to give a red solid. Yield: 53%; ν_{max} (KBr)/cm^{-1} 3540–2480, 1664, 1610, 1595, 1510; Anal. Found: C, 53.58; H, 4.38; N, 11.65. Calc. for $C_{13}H_{10}N_2O_3$ C, 53.71; H, 4.13; N, 11.57%.

4.2.5. Synthesis of 4-[4-(n-decyloxy)phenylazo]benzoic acid (**16**)

This compound was made by adapting a procedure reported previously [14]. Three grams (12.4 mmol) of the compound **15** and 1.0 g (25 mmol) of NaOH were added to a flask and dissolved in a solution of H_2O (40 ml) and EtOH (20 ml). To this solution was added a solution of 1-bromodecane (2.77 g, 12.5 mmol) in 20 ml of EtOH. The reaction mixture was refluxed 24 h. After cooled to the room temperature, the mixture was adjusted to pH 5 using aqueous HCl solution, the red precipitate was filtered and washed several times with water. The product was recrystallized twice in ethanol to give a yellow solid. Yield: 45%; $T_{C-N} = 143.7$, $T_{N-Sc} = 181.1$, $T_{Sc-I} = 245.9$ °C; ν_{max} (KBr)/cm^{-1} 3580–2570, 1684, 1605, 1502, 1285, 1250, 1140; δ_H ($CDCl_3$) 8.10–6.90 (8H, m, ArH), 4.05 (2H, t, *J* 6.6, RCH_2OAr), 1.57–1.20 (16H, m, 8 × CH_2), 0.85 (3H, t, *J* 6.0, CH_3); Anal. Found: C, 72.10; H, 8.13; N, 7.54. Calc. for $C_{23}H_{30}N_2O_3$ C, 72.22; H, 7.90; N, 7.33%.

4.2.6. Synthesis of 2,4-dioxo-3-pentyl 4-[[4-(n-decyloxy)cinnamoyl]oxy] benzoate (**1a**) (general procedure for **2a** and **3a**)

To a solution of the compound **9** (3.04 g, 10 mmol) in 30 ml of anhydrous benzene was added 5 ml of $SOCl_2$ under stirring. The reaction mixture was refluxed for 12 h and concentrated under reduced pressure. The residue was diluted with anhydrous benzene (40 ml). To this solution was added the compound **7** (2.36 g, 10 mmol) and refluxed for 16 h, then the solvent was removed under reduced pressure, the residue was recrystallized twice in anhydrous ethanol to give a white solid. Yield: 82%; ν_{max} (KBr)/cm^{-1} 1726, 1630, 1600, 1505, 1268, 1122; UV–vis λ_{max}/nm (log ε/dm^3 mol^{-1} cm^{-1}) ($CHCl_3$): 320.2 (4.45); δ_H ($CDCl_3$) 8.16–6.96 (8H, m, ArH), 7.84, 6.45 (2H, 2 × d, *J* 16, –CH=CH–), 4.00 (2H, t, *J* 6.6, RCH_2OAr), 14.05, 5.71 (1H, 2 × s, CH), 2.37, 2.07 (6H, 2 × s, 2 × CH_3), 1.88 (2H, m, CH_2), 1.17 (14H, m, 7 × CH_2), 0.88 (3H, t, *J* 6.0, CH_3); *m*/*z* (%): 522 (M^+, 0.12), 288 (100); Anal. Found: C, 71.46; H, 7.17; Calc. for $C_{31}H_{38}O_7$: C, 71.26; H, 7.28%.

4.2.7. Data for 2,4-dioxo-3-pentyl 4-[[4-(n-decyloxy)-cinnamoyl]oxy]cinnate (**2a**)

Yield: 82%; white powder; ν_{max} (KBr)/cm^{-1} 2923, 2853, 1722, 1631, 1600, 1506, 1287, 1252, 1216, 1146; UV–vis λ_{max}/nm (log ε/dm^3 mol^{-1} cm^{-1}) ($CHCl_3$): 321.6 (4.62); δ_H ($CDCl_3$) 14.50, 5.621H, 2 × s, CH), 7.80, 6.54 (2H, 2 × d, *J* 16, –CH=CH–), 7.72, 6.46 (2H, 2 × d, *J* 16, –CH=CH–), 7.62, 7.23 (4H, 2 × d, *J* 8, ArH), 7.52, 6.91 (4H, 2 × d, *J* 8, ArH), 3.99 (2H, t, *J* 6.6, RCH_2OAr), 2.34, 2.05 (2 × s, 6H, 2 × CH_3), 1.78 (m, 2H, CH_2), 1.24 (m, 14H, 7 × CH_2), 0.87 (t, 3H, CH_3); *m*/*z* (%): 548 (M^+, 0.27), 287 (100); Anal. Found: C, 72.31; H, 7.42. Calc. for $C_{33}H_{40}O_7$: C, 72.26; H, 7.30%.

4.2.8. Data for 2,4-dioxo-3-pentyl 4-[[4-(n-decyloxy)-benzoyl]oxy]cinnate (**3a**)

Yield: 68.5%; white powder; ν_{max} (KBr)/cm^{-1} 2927, 2854, 1727, 1635, 1603, 1510, 1258, 1211, 1164, 1064; UV–vis λ_{max}/nm (log ε/dm^3 mol^{-1} cm^{-1}) ($CHCl_3$): 287.4 (4.43); δ_H ($CDCl_3$) 14.50, 5.66 (1H, 2 × s, CH), 8.15, 7.30 (4H, 2 × d, *J* 9, ArH), 7.65, 6.99 (4H, 2 × d, *J* 8.7, ArH), 7.80, 6.58 (2H, 2 × d, *J* 15.9, –CH=CH–), 4.04 (2H, t, *J* 6.6, RCH_2OAr), 2.37, 2.08 (6H, 2 × s, 2 × CH_3), 1.85 (2H, m, CH_2), 1.30 (14H, m, 7 × CH_2), 0.90 (3H, t, *J* 6.0, CH_3); *m*/*z* (%): 522 (M^+, 0.93), 121 (100); Anal. Found: C, 71.11; H, 7.38; Calc. for $C_{31}H_{38}O_7$: C, 71.26; H, 7.28%.

4.2.9. Synthesis of 2,4-dioxo-3-pentyl 4-[[4-(n-decyloxy)benzyl]oxy]benzoate (**4a**) (general procedure for **5a**)

To a suspension of (3.68 g, 10 mmol) in anhydrous DMF (30 ml) was added KOH (0.56 g, 10 mmol), the mixture was stirred at 80 °C for 3 h, then 3-chloro-2,4-pentanedione (1.25 ml, 11 mmol) was added to the above mixture and stirred over night at 50 °C. After it cooled to ambient temperature, 100 ml water was added to the reaction mixture and the mixture was extracted three times with $CHCl_3$. The combined extracts were washed with water for three times and then dried with sodium sulfate. The solvent was evaporated under reduced pressure and the residue was purified by chromatography on silica gel using ethyl acetate: petroleum ether (60–90 °C) (1:2) as eluant. The products were recrystallized from EtOH to give a white needle crystal. Yield: 72.8%; ν_{max} (KBr)/cm^{-1} 2920, 2853, 1728, 1711, 1607, 1514, 1246, 1168; UV–vis λ_{max}/nm (log ε/dm^3 mol^{-1} cm^{-1}) ($CHCl_3$): 263.6 (4.31); δ_H ($CDCl_3$) 8.05, 6.89 (4H, 2 × d, *J* 9.6, ArH), 7.32, 7.01 (4H, 2 × d, *J* 8.8, ArH), 5.67 (1H, s, CH), 5.04 (2H, s, $ArCH_2OAr$), 3.94 (2H, t, *J* 6.6, RCH_2OAr), 2.37 (6H, s, 2 × CH_3), 1.79 (2H, m, CH_2), 1.27 (14H, m, 7 × CH_2), 0.87 (3H, t, *J* 6.0, CH_3); *m/z* (%): 482 (M^+, 0.78), 366 (76.51), 57 (100); Anal. Found C, 72.06; H, 7.80; Calc. for $C_{29}H_{38}O_6$: C, 72.20; H, 7.88%.

4.2.10. Data for 2,4-dioxo-3-pentyl 4-[4-(n-decyloxy)phenylazo]benzoate (**5a**)

Yield: 60%; red solid; ν_{max} (KBr)/cm^{-1} 2957, 2865, 1730, 1630, 1598, 1505, 1260, 1255, 1140; UV–vis λ_{max}/nm (log ε/dm^3 mol^{-1} cm^{-1}) ($CHCl_3$): 361.5 (4.46); δ_H ($CDCl_3$) 14.45, 5.70 (1H, 2 × s, CH), 8.20–7.10 (8H, m, ArH), 4.15 (2H, t, *J* 6.6, RCH_2OAr), 2.38, 2.05 (6H, 2 × s, 2 × CH_3), 1.87 (2H, m, CH_2), 1.18 (14H, m, 7 × CH_2), 0.86 (3H, t, *J* 6.0, CH_3); Anal. Found: C, 70.17; H, 7.81; N, 5.74. Calc. for $C_{28}H_{36}N_2O_5$: C, 69.98; H, 7.55; N, 5.83%.

4.2.11. Synthesis of dicarbonyl-2,4-dioxo-3-pentyl-4-[4-(n-decyloxy)cinnamoyl]oxy] benzoatorhodium(I) (**1b**) (general procedure [9] for **2b**–**5b**)

A mixture of acetone solution of **1a** (109.6 mg, 0.2 mmol) and $[RhCl(CO)_2]_2$ [23] (38.9 mg, 0.1 mmol) with excess of solid barium carbonate was stirred under an argon atmosphere at room temperature for 2 h. Then the reaction mixture was filtered to remove the precipitate, the filtrate was evaporated under reduced pressure. The reminder was purified by silica gel using chloroform as eluant and further purified by recrystallization in EtOH to give a yellow solid. Yield: 79.9%; ν_{max} (KBr)/cm^{-1} 2930, 2854, 2082, 2009, 1725, 1634, 1603, 1511, 1265, 1208, 1148; UV–vis λ_{max}/nm (log ε/dm^3 mol^{-1} cm^{-1}) ($CHCl_3$): 321.0 (4.50); δ_H ($CDCl_3$) 8.30, 7.38 (4H, 2 × d, *J* 8.8, ArH), 7.90, 6.56 (2H, 2 × d, *J* 16, –CH=CH–), 7.58, 7.00 (4H, 2 × d, *J* 8.4, ArH), 4.10 (2H, t, *J* 6.6, RCH_2OAr), 2.14 (6H, s, 2 × CH_3), 1.78 (2H, m, CH_2), 1.26 (14H, m, 7 × CH_2), 0.86 (3H, t, *J* 6.0, CH_3); Anal. Found C, 57.92; H, 5.59; Calc. for $C_{33}H_{37}RhO_9$: C, 58.23; H, 5.44%.

4.2.12. Data for dicarbonyl-2,4-dioxo-3-pentyl 4-[[4-(n-decyloxy)cinnamoyl]oxy] cinnatorhodium(I) (**2b**)

Yellow solid, yield: 75.3%; ν_{max} (KBr)/cm^{-1} 2925, 2860, 2081, 2009, 1723, 1631, 1601, 1509, 1473, 1253, 1139; UV–vis λ_{max}/nm (log ε/dm^3 mol^{-1} cm^{-1}) ($CHCl_3$): 323.0 (4.68); δ_H ($CDCl_3$) 8.20, 7.42 (4H, 2 × d, *J* 8.8, Ar), 7.82, 6.50 (2H, 2 × d, *J* 16, –CH=CH–), 7.68, 6.48 (2H, 2 × d, *J* 16, –CH=CH–), 7.56, 6.94 (4H, 2 × d, *J* 8.4, Ar), 4.05 (2H, t, *J* 6.6, RCH_2OAr), 2.10 (6H, s, 2 × CH_3), 1.76 (2H, m, CH_2), 1.26 (14H, m, 7 × CH_2), 0.88 (3H, t, *J* 6.0, CH_3); Anal. Found: C, 59.72; H, 5.43. Calc. for $C_{35}H_{39}RhO_7$: C, 59.49; H, 5.52%.

4.2.13. Data for dicarbonyl-2,4-dioxo-3-pentyl 4-[[4-(n-decyloxy)benzoyl]oxy] cinnatorhodium(I) (**3b**)

Yellow solid, yield: 72.8%; ν_{max} (KBr)/cm^{-1} 2082, 2009, 1725, 1634, 1603, 1585, 1511, 1474, 1265, 1148; UV–vis λ_{max}/nm (log ε/dm^3 mol^{-1} cm^{-1}) ($CHCl_3$): 288.0 (4.48); δ_H ($CDCl_3$) 8.12, 7.30 (4H, 2 × d, *J* 8.8, Ar), 7.88, 6.56 (2H, 2 × d, *J* 16, –CH=CH–), 7.62, 6.96 (4H, 2 × d, *J* 8.4, Ar), 4.03 (2H, t, *J* 6.6, RCH_2OAr), 2.07 (6H, s, 2 × CH_3), 1.80 (2H, m, CH_2), 1.22 (14H, m, 7 × CH_2), 0.87 (3H, t, *J* 6.0, CH_3); Anal. Found: C, 58.41; H, 5.53. Calc. for $C_{31}H_{37}O_7Rh$: C, 58.23; H, 5.44%.

4.2.14. Data for dicarbonyl-2,4-dioxo-3-pentyl 4-[[4-(n-decyloxy)benzyl]oxy]benzoato-rhodium(I) (**4b**)

Yellow solid; yield: 72.3%; ν_{max} (KBr)/cm^{-1} 2081, 2008, 1734, 1609, 1585, 1472, 1245, 1151; UV–vis λ_{max}/nm (log ε/dm^3 mol^{-1} cm^{-1}) ($CHCl_3$): 267.5 (4.45); δ_H ($CDCl_3$) 8.12, 6.90 (4H, 2 × d, *J* 9.6, Ar), 7.30, 7.04 (4H, 2 × d, *J* 8.8, Ar), 5.10 (s, 2H, $ArCH_2OAr$), 4.03 (2H, t, *J* 6.6, RCH_2OAr), 2.16 (6H, s, 2 × CH_3), 1.76 (2H, m, CH_2), 1.24 (14H, m, 7 × CH_2), 0.86 (3H, t, *J* 6.0, CH_3); Anal. Found: C, 58.36; H, 5.87. Calc. for $C_{31}H_{37}O_7Rh$: C, 58.13; H, 5.78%.

4.2.15. Data for dicarbonyl-2,4-dioxo-3-pentyl 4-[4-(n-decyloxy)phenylazo] benzoato-rhodium(I) (**5b**)

Red solid; yield: 75.8%; ν_{max} (KBr)/cm^{-1} 2950, 2860, 2080, 2012, 1737, 1605, 1505, 1585, 1417, 1260, 1250, 1145; UV–vis λ_{max}/nm (log ε/dm^3 mol^{-1} cm^{-1}) ($CHCl_3$): 363.2 (4.49); δ_H ($CDCl_3$) 8.25–6.95 (8H, m, ArH), 4.00 (2H, t, *J* 6.6, $ArOCH_2$), 2.07 (6H, s, 2 × CH_3), 1.90 (2H, m, CH_2), 1.22 (14H, m, 7 × CH_2), 0.83 (3H, t, *J* 6.0, CH_3); Anal. Found: C, 56.08; H, 5.85; N, 4.66; Calc. for $C_{30}H_{35}N_2RhO_7$: C, 56.43; H, 5.48; N, 4.39%.

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