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Catalytic performance of a Keplerate-type, giant-ball nanoporous isopolyoxomolybdate as a highly efficient recyclable catalyst for the synthesis of biscoumarins

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Abstract: In continuation of our previous works on the application of $(NH_4)_{42}[Mo^{VI}_{72}Mo^{V}_{60}O_{372}(CH_3COO)_{30}(H_2O)_{72}]$, a Keplerate-type giant-ball nanoporous isopolyoxomolybdate, as a catalyst for a series of organic transformations, in this paper, we discovered that this new attractive catalyst has high catalytic activity in the synthesis of biscoumarins prepared by the reaction of 4-hydroxycoumarin and aromatic or aliphatic aldehydes in refluxing ethanol. The catalyst was prepared according to a previously published literature procedure using inexpensive and readily available starting materials. Furthermore, the catalyst could be recovered conveniently and reused efficiently such that a considerable catalytic activity still could be achieved after fifth run. Other beneficial features of this new synthetic approach include short reaction time, high yields, clean reaction profiles, and a simple work-up procedure.

Keywords: biscoumarin; giant-ball nanoporous isopolyoxomolybdate; Keplerate; $\{Mo_{132}\}$.

1 Introduction

The development of heterogeneous catalysts and how they affect specific transformations in chemical synthesis has become a major area of research. The potential advantages of these materials over homogeneous systems, in terms of their simplified recovery and reusability, could potentially allow for the development of environmentally benign chemical procedures in both academic and industrial settings. Catalysts of this type have the potential to make the processes in which they are applied cleaner, safer, higher-yielding, and relatively inexpensive [1–4]. Polyoxometalates (POMs) are a large family of metal-oxygen clusters of early transition metals. These compounds have stimulated many current research activities in a broad range of fields such as catalysis, magnetism, materials science and biomedicine [5–8]. Such a stimulation is due to diverse and highly modifiable sizes, shapes, charge densities, acidities and reversible redox potentials of POMs [9, 10]. In recent years, the synthesis of nanotubular materials consisting of POMs such as POMs-including titania nanotubes [11] and POMs-organic hybrid nanotubes [12] has been a subject of increasing interest. These new types of nanotubes show not only the functional properties of POMs but also the advantages of tubular systems in the application, for example, of catalytic and photochemical properties [11–13].

Giant nanosized porous Keplerate-type POMs, reported for the first time by Müller and co-workers [14], show a large variety of applications in fundamental and applied science, such as in modeling passive cation transport through membranes, encapsulation, nanoseparation chemistry, and magnetic and optics properties [15, 16]. In spite of these valuable properties, to the authors' knowledge, there are only three references in the literature on the use of giant nanosized porous POMs as a catalyst in organic transformations [17–19].

Coumarins are a large group of heterocycles with diverse and interesting biological activities. These compounds are reported to possess significant anticoagulant, insecticidal, antihelminthic, hypnotic, antifungal, and HIV protease inhibition activities [20–24]. Biscoumarins, the bridge substituted dimers of 4-hydroxycoumarin, have enormous potential as anticoagulants [25, 26]. A number of biscoumarins have also been found to be urease inhibitors [27].

These compounds are generally synthesized via the reaction of 4-hydroxycoumarin with aldehydes in the presence of various Brønsted and Lewis acidic catalysts

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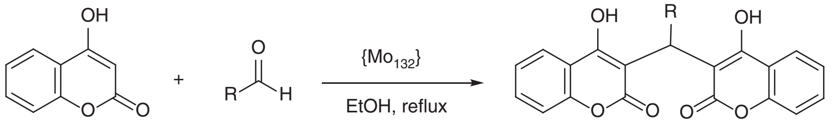


1 **2a–l** **3a–l**

Scheme 1: $\{Mo_{132}\}$ catalyzed synthesis of biscoumarins ($\{Mo_{132}\} \equiv (NH_4)_{42}[Mo^{VI}_{72}Mo^{V}_{60}O_{372}(CH_3COO)_{30}(H_2O)_{72}]$).

such as Brønsted-acidic ionic liquids based on ammonium [28], imidazolium [29], and benzimidazolium [30] cations, $[P_4VPy\text{-}BuSO_3H]HSO_4$, a supported acidic ionic liquid [31], $TiO_2\text{-}SO_3H$ [32], tetrabutylammonium hexatungstate $[TBA]_2[W_6O_{19}]$ [33], $RuCl_3{\cdot}nH_2O$ [34], I_2 [35], and sulfonated rice husk ash ($RHA\text{-}SO_3H$) [36]. Catalyst-free synthesis of these compounds with long reaction times has also been reported [37].

During the course of our recent studies directed towards the development of practical and environmentally friendly procedures for the synthesis of organic compounds using reusable catalysts [38–46], we investigated the application of $(NH_4)_{42}[Mo^{VI}_{72}Mo^{V}_{60}O_{372}(CH_3COO)_{30}(H_2O)_{72}]$, a Keplerate-type giant-ball nanoporous isopolyoxomolybdate denoted as $\{Mo_{132}\}$, as a catalyst for a series of organic transformations. This new reusable catalyst performed well and showed a high level of catalytic activity in the synthesis of 1,2,4,5-tetrasubstituted imidazoles, 1,8-dioxo-octahydroxanthenes and 1,8-dioxodecahydroacridines [18, 19]. This fact prompted us to investigate the catalytic activity of this material in the synthesis of biscoumarins (Scheme 1). For the first time, this ball-shaped POM has been characterized using the transmission electron microscopy (TEM) image by Polarz et al. [47]. The TEM picture clearly shows a periodic structure with an average size of approximately 3 nm in diameter. This experimentally obtained diameter fits nicely with the theoretical value for the inner diameter of this ball-shaped POM that was calculated to be 2.9 nm [14, 48].

Table 1: Optimization of reaction conditions for the synthesis of compound **3e** catalyzed by $\{Mo_{132}\}$.[a]

Entry	Catalyst (g)	Solvent	*T* (°C)	Time (min)	Isolated yield (%)
1	None	H_2O	Reflux	90	10
2	None	EtOH	Reflux	90	17
3	0.07	Solvent-free	110	45	27
4	0.07	Solvent-free	130	45	29
5	0.02	H_2O	Reflux	50	14
6	0.04	H_2O	Reflux	45	32
7	0.06	H_2O	Reflux	30	69
8	0.07	H_2O	Reflux	30	81
9	0.02	EtOH	Reflux	45	23
10	0.04	EtOH	Reflux	20	52
11	0.06	EtOH	Reflux	15	88
12	0.07	EtOH	Reflux	10	97
13	0.07	EtOH	50	25	89
14	0.07	EtOH	r.t.	30	83
15	0.08	EtOH	Reflux	20	97
16	0.02	MeOH	Reflux	45	15
17	0.04	MeOH	Reflux	40	38
18	0.06	MeOH	Reflux	30	77
19	0.07	MeOH	Reflux	25	85
20	0.02	$CHCl_3$	Reflux	45	16
21	0.04	$CHCl_3$	Reflux	35	41
22	0.06	$CHCl_3$	Reflux	30	78
23	0.07	$CHCl_3$	Reflux	25	89
24	0.02	CH_3CN	Reflux	60	10
25	0.04	CH_3CN	Reflux	50	28
26	0.06	CH_3CN	Reflux	35	63
27	0.07	CH_3CN	Reflux	25	76

[a] Reaction conditions: 4-hydroxycoumarin (**1**) (2 mmol) and 4-cholorobenzaldehyde (**2e**) (1 mmol).

2 Results and discussion

The catalyst $\{Mo_{132}\}$ was characterized by FT-IR and UV/Vis spectroscopy as reported in our previous work [19]. At the beginning of this study, 4-chlorobenzaldehyde (**2e**) was employed as the model aldehyde and reacted with 4-hydroxycoumarin (**1**). In order to get the effective reaction conditions, the reaction was optimized in terms of various parameters such as catalyst amount, effect of solvent and influence of temperature (Table 1). Low yields of the product **3e** were obtained in the absence of the catalyst in refluxing EtOH or H_2O (entries 1 and 2) or in the presence of the catalyst under solvent-free conditions at high temperatures (entries 3 and 4), indicating that the catalyst and solvent are necessary for the reaction. As can be seen from Table 1, among the tested solvents such as H_2O, EtOH, MeOH, $CHCl_3$, CH_3CN, and also solvent-free conditions and various amounts of the catalyst, the reaction was more facile and proceeded to give the highest yield, using 0.07 g of $\{Mo_{132}\}$ in EtOH at reflux temperature (entry 12). All subsequent reactions were carried out in these optimized conditions.

Encouraged by the remarkable results obtained with the above reaction conditions, and in order to show the generality and scope of this new protocol, we extended the reaction of 4-hydroxycoumarin (**1**) with a range of other aromatic or aliphatic aldehydes **2a–l** under the optimized reaction conditions, and the results are summarized in Table 2. As shown, all reactions proceed very cleanly to give the corresponding biscoumarins **3a–l** in high yields over short reaction times. Purity checks with melting points, TLC and the ^{1}H NMR spectroscopic data reveal that only one product is formed in all cases and no undesirable side products are observed. The structures of all known products **3a–l** were deduced from their ^{1}H NMR and FT-IR spectral data and a comparison of their melting points with those of authentic samples. For example, as shown in Fig. 1, the ^{1}H NMR spectrum of **3f** in $CDCl_3$ showed a sharp ^{1}H NMR signal at $\delta = 6.09$ ppm for the methine proton along with two sharp singlets in the down-field region of the spectrum at $\delta = 11.35$ and 11.57 ppm for hydroxyl groups as well as the signals in the aromatic region due to 12 aromatic protons, indicating the formation of the compound **3f**.

To test the recyclability of $\{Mo_{132}\}$, after completion of the model reaction, the catalyst was recovered according to the procedure described in the Experimental section. The separated catalyst was dried at 60 °C under vacuum for 1 h before being reused in a similar reaction. The catalyst could be used at least five times without changing the yield of the product significantly (97 % for 1st use; 97 % for 2nd use; 96 % for 3rd use; 95 % for 4th use; 93 % for 5th use). Furthermore, the FT-IR spectra of the recovered catalyst (Fig. 2b–e) were almost identical to that of the fresh catalyst (Fig. 2a), which indicated that the structure of the catalyst was unchanged by the reaction.

Although we did not investigate the reaction mechanism, a plausible mechanism for this reaction may proceed as depicted in Scheme 2. On the basis of our previous reports [18, 19], it is reasonable to assume that several accessible Mo sites and NH_4 groups in $\{Mo_{132}\}$ could act as Lewis acid and Brönsted acid centers, respectively, and therefore promote the necessary reactions. The catalyst would play a significant role in increasing the electrophilic character of the electrophiles in the reaction. According to this mechanism, the $\{Mo_{132}\}$ catalyst would facilitate the formation of intermediates **I**, **II** and **III**. Under these conditions, however, attempts to isolate the proposed intermediates failed even after careful monitoring of the reactions.

3 Conclusion

In conclusion, in this paper, we showed that $\{Mo_{132}\}$, a Keplerate-type giant-ball nanoporous isopolyoxomolybdate, as a highly effective heterogeneous catalyst effectively catalyzes the reaction of 4-hydroxycoumarin and aromatic or aliphatic aldehydes in refluxing ethanol. This method provided the biscoumarins products in high yields over short reaction time, following a facile work-up process. The catalyst is inexpensive and easily obtained, stable and storable, easily recycled and reused for several cycles with consistent activity.

Table 2: $\{Mo_{132}\}$ catalyzed synthesis of biscoumarins.[a]

Entry	R	Products[b]	Time (min)	Isolated yield (%)	M.p. (°C)	
					Found	Reported
1	C_6H_5	**3a**	13	92	231–233	226–229 [29]
2	3-BrC_6H_4	**3b**	10	95	286–288	Not reported [36]
3	4-BrC_6H_4	**3c**	12	95	264–267	263–266 [29]
4	2-ClC_6H_4	**3d**	12	93	204–205	201–203 [30]
5	4-ClC_6H_4	**3e**	10	97	253–255	252–254 [32]
6	4-FC_6H_4	**3f**	8	95	213–214	214.5 [37]
7	4-MeC_6H_4	**3g**	13	93	269–271	266–269 [30]
8	4-$MeOC_6H_4$	**3h**	8	93	246–248	250–252 [30]
9	3-$O_2NC_6H_4$	**3i**	8	96	233–236	236–238 [34]
10	4-$O_2NC_6H_4$	**3j**	8	94	232–234	233–235 [34]
11	2-Thienyl	**3k**	11	97	210–212	206–209 [35]
12	n-Pr	**3l**	14	92	143–145	144–146 [32]

[a] Reaction conditions: 4-hydroxycoumarin (**1**) (2 mmol), aldehyde **2a–l** (1 mmol), $\{Mo_{132}\}$ (0.07 g), EtOH (5 mL), reflux.
[b] All the products were characterized by their FT-IR and ^{1}H NMR spectral data and by comparison of their melting points with those of authentic samples.

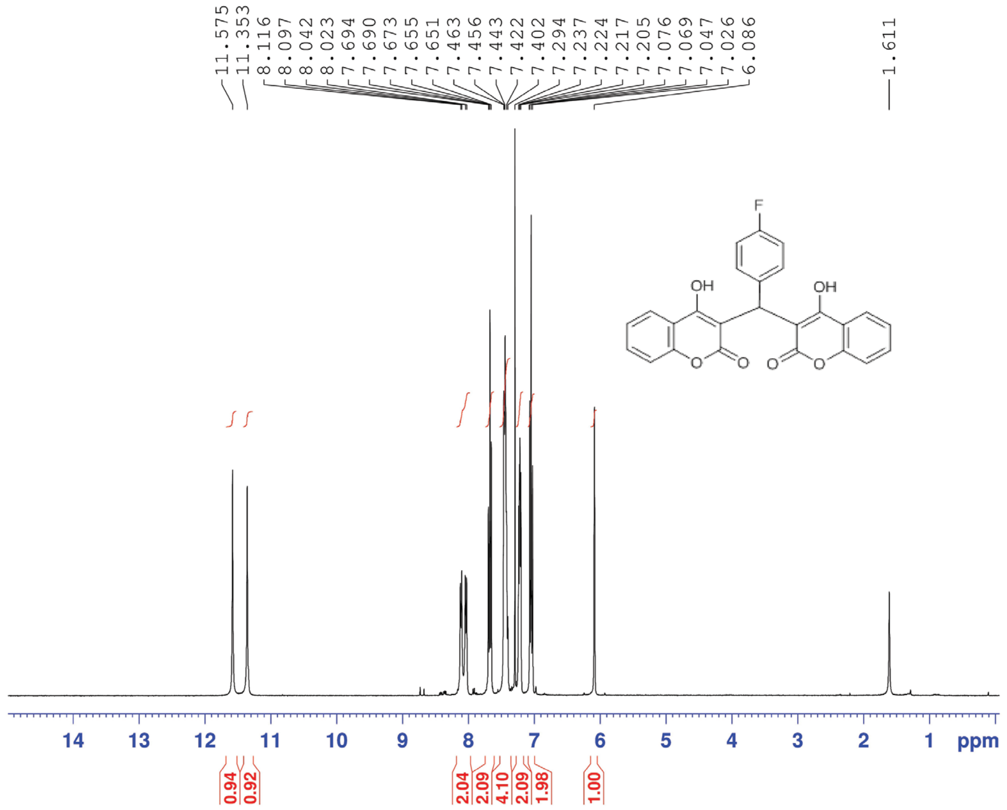


Fig. 1: The ^{1}H NMR spectrum of compound **3f** in $CDCl_3$.

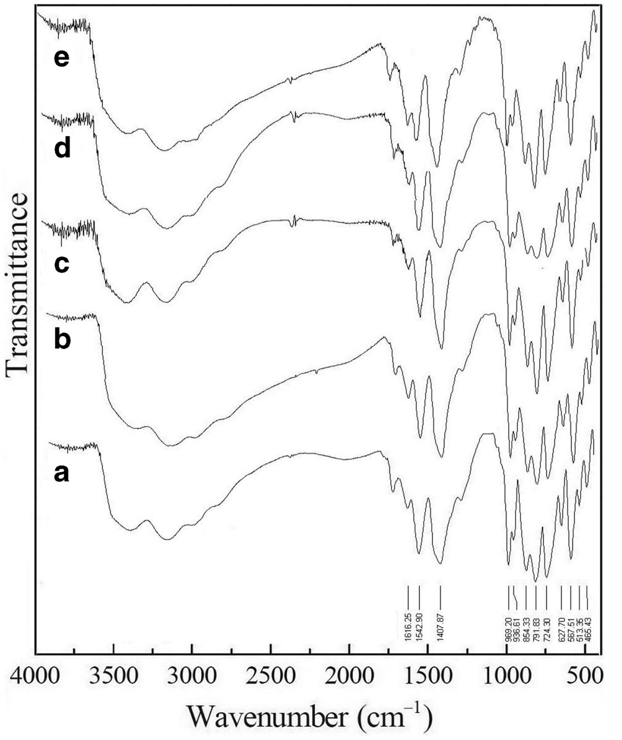


Fig. 2: FT-IR spectra of a fresh catalyst $\{Mo_{132}\}$ (run 1, a) and recovered catalysts (runs 2–5, b–e) for the synthesis of compound **3e** in the model reaction.

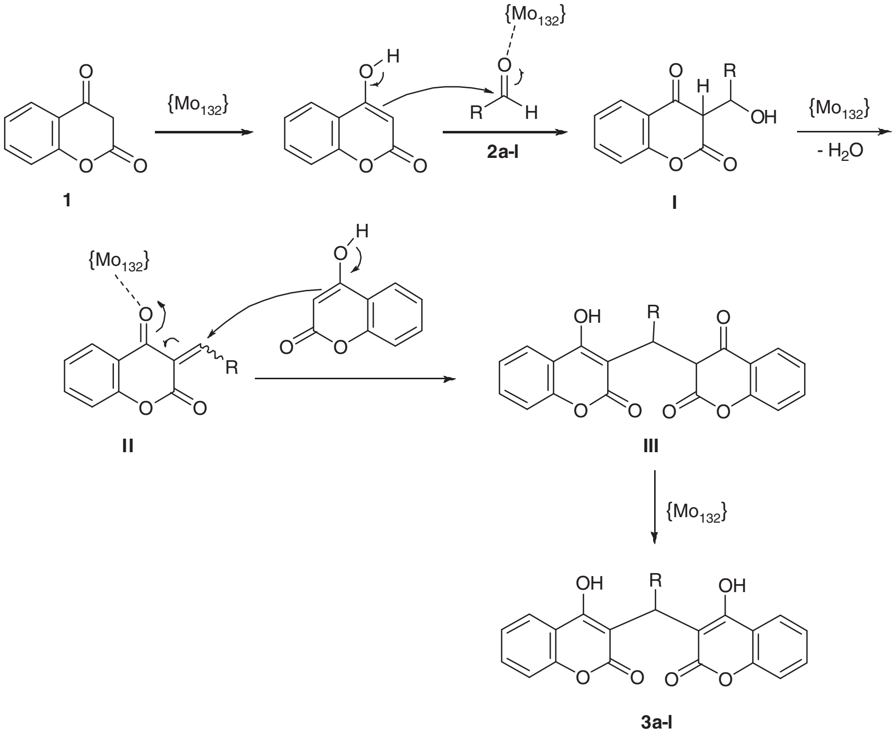
4 Experimental section

4.1 Chemicals and apparatus

All chemicals were available commercially and used without additional purification. The catalyst was synthesized according to the literature. Melting points were recorded using a Stuart SMP3 melting point apparatus. The FT-IR spectra of the products were obtained with KBr disks, using a Tensor 27 Bruker spectrophotometer. The ^{1}H NMR (400 and 500 MHz) spectra were recorded using Bruker 400 and 500 spectrometers.

4.2 General experimental procedure for the synthesis of biscoumarins 3a–l catalyzed by $\{Mo_{132}\}$

A mixture of 4-hydroxycoumarin (**1**) (2 mmol), aromatic or aliphatic aldehyde **2a–l** (1 mmol), $\{Mo_{132}\}$ (0.07 g) as a catalyst in ethanol (5 mL) was heated under reflux for the appropriate time. The reaction was monitored by TLC. Upon completion of the transformation, the catalyst was removed by filtration of the hot suspension. The catalyst



Scheme 2: Plausible mechanism for the $\{Mo_{132}\}$-catalyzed formation of biscoumarins **3a–l**.

was washed with a small portion of hot ethanol. After cooling, the combined filtrate was allowed to stand at room temperature. The precipitated solid was collected by filtration, and recrystallized from ethanol to give compounds **3a–l** in high yields.

4.3 FT-IR and ^{1}H NMR data

4.3.1 3,3′-(Phenylmethylene)bis(4-hydroxy-2H-chromen-2-one) (3a) (Table 2, entry 1)

IR (KBr disk): ν = 3430, 3059, 1672, 1618, 1562, 1493, 1352, 1098, 761 cm^{-1}. – ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 6.14 (s, 1H, CH), 7.25–7.50 (m, 9H, arom-H), 7.64–7.70 (m, 2H, arom-H), 8.00–8.14 (m, 2H, arom-H), 11.33 (s, 1H, OH), 11.57 (s, 1H, OH).

4.3.2 3,3′-((3-Bromophenyl)methylene)bis(4-hydroxy-2H-chromen-2-one) (3b) (Table 2, entry 2)

IR (KBr disk): ν = 3434, 3069, 1664, 1610, 1566, 1498, 1471, 1353, 1312, 1099, 764 cm^{-1}. – ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 6.09 (s, 1H, CH), 7.15–7.50 (m, 9H, arom-H), 7.65–7.72 (m, 2H, arom-H), 8.05 (d, J = 8.0 Hz, 1H, arom-H), 8.11 (d, J = 8.0 Hz, 1H, arom-H), 11.33 (s, 1H, OH), 11.61 (s, 1H, OH).

4.3.3 3,3′-((4-Bromophenyl)methylene)bis(4-hydroxy-2H-chromen-2-one) (3c) (Table 2, entry 3)

IR (KBr disk): ν = 3432, 3071, 1666, 1616, 1558, 1491, 1354, 1096, 762 cm^{-1}. – ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 6.04 (s, 1H, CH), 7.12 (dd, J = 8.6, 1.2 Hz, 2H, arom-H), 7.37–7.48 (m, 6H, arom-H), 7.63–7.69 (m, 2H, arom-H), 8.00–8.12 (m, 2H, arom-H), 11.33 (s br, 1H, OH), 11.56 (s br, 1H, OH).

4.3.4 3,3′-((2-Chlorophenyl)methylene)bis(4-hydroxy-2H-chromen-2-one) (3d) (Table 2, entry 4)

IR (KBr disk): ν = 3436, 3074, 1650, 1565, 1497, 1471, 1454, 1353, 1307, 1277, 1101, 767 cm^{-1}. – ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 6.17 (s, 1H, CH), 7.24–7.45 (m, 7H, arom-H), 7.48 (d, J = 7.2 Hz, 1H, arom-H), 7.64 (td, J = 7.8, 1.2 Hz, 2H, arom-H), 8.00–8.10 (m, 2H, arom-H), 10.96 (br, 1H, OH), 11.67 (s br, 1H, OH).

4.3.5 3,3′-((4-Chlorophenyl)methylene)bis(4-hydroxy-2H-chromen-2-one) (3e) (Table 2, entry 5)

IR (KBr disk): ν = 3429, 3072, 1668, 1618, 1562, 1491, 1454, 1351, 1310, 1094, 766 cm^{-1}. – ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 6.06 (s, 1H, CH), 7.18 (dd, J = 8.8, 0.8 Hz, 2H, arom-H), 7.31 (d, J = 8.8 Hz, 2H, arom-H), 7.38–7.47 (m, 4H, arom-H), 7.63–7.69 (m, 2H, arom-H), 8.01 (d, J = 7.6 Hz, 1H, arom-H), 8.09 (d, J = 7.6 Hz, 1H, arom-H), 11.35 (s br, 1H, OH), 11.56 (s br, 1H, OH).

4.3.6 3,3′-((4-Fluorophenyl)methylene)bis(4-hydroxy-2H-chromen-2-one) (3f) (Table 2, entry 6)

IR (KBr disk): ν = 3458, 3066, 1672, 1562, 1507, 1453, 1352, 1310, 1102, 765 cm^{-1}. – ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 6.09 (s, 1H, CH), 7.05 (t, J = 8.4 Hz, 2H, arom-H), 7.20–7.25 (m, 2H, arom-H), 7.40–7.50 (m, 4H, arom-H), 7.67 (td, J = 8.0, 1.6 Hz, 2H, arom-H), 8.03 (d, J = 7.6 Hz, 1H, arom-H), 8.11 (d, J = 7.6 Hz, 1H, arom-H), 11.35 (s, 1H, OH), 11.57 (s, 1H, OH).

4.3.7 3,3′-((4-Methylphenyl)methylene)bis(4-hydroxy-2H-chromen-2-one) (3g) (Table 2, entry 7)

IR (KBr disk): ν = 3423, 3057, 2998, 1671, 1605, 1564, 1493, 1352, 1309, 1095, 764 cm^{-1}. – ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 2.36 (s, 3H, CH_3), 6.09 (s, 1H, CH), 7.14 (AB_q, J_{AB} = 8.4 Hz, 4H, arom-H), 7.38–7.45 (m, 4H, arom-H), 7.65 (td, J = 8.6, 1.6 Hz, 2H, arom-H), 8.02 (d br, J = 7.2 Hz, 1H, arom-H), 8.09 (d br, J = 7.2 Hz, 1H, arom-H), 11.34 (s br, 1H, OH), 11.53 (s br, 1H, OH).

4.3.8 3,3′-((4-Methoxyphenyl)methylene)bis(4-hydroxy-2H-chromen-2-one) (3h) (Table 2, entry 8)

IR (KBr disk): ν = 3427, 3002, 1671, 1605, 1564, 1510, 1353, 1259, 1094, 769 cm^{-1}. – ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ = 3.83 (s, 3H, OCH_3), 6.08 (s, 1H, CH), 6.87 (d, 2H, J = 8.7 Hz, arom-H), 7.16 (d, 2H, J = 8.7 Hz, arom-H), 7.40–7.50 (m, 4H, arom-H), 7.65 (t, 2H, J = 7.9 Hz, arom-H), 8.04 (s br, 1H, arom-H), 8.09 (s br, 1H, arom-H), 11.32 (s, 1H, OH), 11.54 (s, 1H, OH).

4.3.9 3,3′-((3-Nitrophenyl)methylene)bis(4-hydroxy-2H-chromen-2-one) (3i) (Table 2, entry 9)

IR (KBr disk): ν = 3417, 3059, 1673, 1605, 1562, 1493, 1446, 1352, 1309, 1098, 760 cm^{-1}. – ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 6.16 (s, 1H, CH), 7.40–7.50 (m, 4H, arom-H), 7.55 (t, J = 8.0 Hz, 1H, arom-H), 7.60–7.75 (m, 3H, arom-H), 8.03 (d, J = 8.0 Hz, 1H, arom-H), 8.10–8.20 (m, 3H, arom-H), 11.42 (s, 1H, OH), 11.61 (s, 1H, OH).

4.3.10 3,3′-((4-Nitrophenyl)methylene)bis(4-hydroxy-2H-chromen-2-one) (3j) (Table 2, entry 10)

IR (KBr disk): ν = 3413, 3060, 1663, 1600, 1564, 1522, 1491, 1453, 1352, 1313, 1099, 786 cm^{-1}. – ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 6.14 (s, 1H, CH), 7.40–7.50 (m, 6H, arom-H), 7.70 (t, J = 7.6 Hz, 2H, arom-H), 8.02 (d, J = 7.6 Hz, 1H, arom-H), 8.11 (d, J = 8.0 Hz, 1H, arom-H), 8.21 (d, J = 8.8 Hz, 2H, arom-H), 11.40 (s, 1H, OH), 11.60 (s, 1H, OH).

4.3.11 3,3′-(Thiophen-2-ylmethylene)bis(4-hydroxy-2H-chromen-2-one) (3k) (Table 2, entry 11)

IR (KBr disk): ν = 3429, 3068, 1661, 1565, 1496, 1452, 1346, 1309, 1267, 1216, 1098, 761 cm^{-1}. – ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 6.23 (s, 1H, CH), 6.88–6.91 (m, 1H, arom-H), 6.97–7.00 (m, 1H, arom-H), 7.25 (dt, J = 5.2, 1.2 Hz, 1H, arom-H), 7.40–7.48 (m, 4H, arom-H), 7.66 (td, J = 8.6, 1.6 Hz, 2H, arom-H), 8.06 (d br, J = 7.2 Hz, 1H, arom-H), 8.09 (d br, J = 7.2 Hz, 1H, arom-H), 11.32 (s, 1H, OH), 11.83 (s, 1H, OH).

4.3.12 3,3′-(Butane-1,1-diyl)bis(4-hydroxy-2H-chromen-2-one) (3l) (Table 2, entry 12)

IR (KBr disk): ν = 3460, 3060, 1687, 1615, 1537, 1460, 1406, 1376, 1353, 1179, 1107, 755 cm^{-1}. – ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.97 (t, J = 7.2 Hz, 3H, CH_3), 1.37 (sex, J = 7.2 Hz, 2H, CH_2), 2.30–2.50 (m, 2H, CH_2), 4.53 (t, J = 8.0 Hz, 1H, CH), 7.35–7.42 (m, 4H, arom-H), 7.58–7.64 (m, 2H, arom-H), 8.02 (dd, J = 8.2, 1.2 Hz, 2H, arom-H), 11.23 (s, 1H, OH), 12.06 (s, 1H, OH).

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Graphical synopsis

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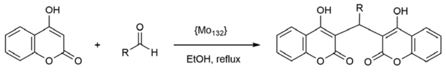

$\{Mo_{132}\} \equiv (NH_4)_{42}[Mo^{VI}{}_{72}Mo^{V}{}_{60}O_{372}(CH_3COO)_{30}(H_2O)_{72}]$