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ORIGINAL PAPER

Choline chloride and itaconic acid-based deep eutectic solvent as an efficient and reusable medium for the preparation of 13-aryl-5*H*-dibenzo[*b,i*]xanthene-5,7,12,14(13*H*)-tetraones

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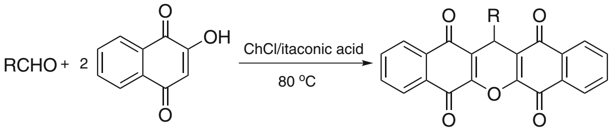
Abstract Choline chloride and itaconic acid-based deep eutectic solvent has been identified as an effective catalyst and reaction medium for synthesis of 13-aryl-5*H*-dibenzo[*b,i*]xanthene-5,7,12,14(13*H*)-tetraones by condensation of 2-hydroxynaphthalene-1,4-dione with various aldehydes. The reaction conditions are mild and environmentally friendly.

Graphical abstract



Keywords Deep eutectic solvents · Low melting mixtures · Choline chloride/itaconic acid · Xanthene derivatives

Introduction

Xanthene and their derivatives are an important class of heterocyclic compounds that exhibit broad spectra of pharmaceutical and biological properties, such as antimicrobial [1], antiproliferative [2], antibacterial [3], and antioxidant activity [4]. Xanthenes can also be used in the preparation of stable laser dyes [5], fluorescent sensor [6, 7], and protein labelling fluorophores [8]. Consequently, various well-designed methodologies have been developed to assemble these interesting scaffolds. In particular, the construction of 13-aryl-5*H*-dibenzo[*b,i*]xanthene-5,7,12,14-(13*H*)-tetraones has been conventionally accomplished by reaction of aldehydes with 2-hydroxynaphthalene-1,4-dione in the presence of various catalysts, such as poly(4-vinylpyridinium) hydrogensulfate [9], *p*-toluenesulfonic acid [10, 11], starch sulphate [12], phosphoric acid supported on alumina (H_3PO_4/Al_2O_3) [13], *N*-sulfonic acid poly(4-vinylpyridinium) hydrogensulfate [14], and ionic liquids [15–20]. Due to their manifold applications, the development of a novel methodology for synthesis of xanthenes will be a valuable contribution to this class heterocycles.

In recent years, a new family of solvents, so-called deep eutectic solvents (DESs) or low melting mixtures (LMMs), has been emerged in organic transformations [21] and other research fields as reviewed in the literatures [22–25]. They are prepared by mixing phosphonium or quaternary ammonium salt such as choline chloride (ChCl) with hydrogen-bond donors such as acids, alcohols, amines, or carbohydrates without any further purification steps, which form a liquid by hydrogen-bond interactions. The properties of DESs are similar to that of conventional ionic liquids in terms of undetectable vapour pressure, wide liquid temperature range, good solubility for many organic or inorganic compounds, and the feasibility for designing. The ease of preparation, availability, cost effectiveness, stability, less toxicity, and biodegradability make these DESs versatile alternatives to ionic liquids. In view of some previous works [26–38] and our recent research programme on the development of novel and environmentally benign synthetic methodologies [39–45], herein we report ChCl/itaconic acid as reaction medium and catalyst for the synthesis of 13-aryl-5*H*-dibenzo[*b,i*]xanthene-5,7,12,14(13*H*)-tetraones by condensation of 2-hydroxynaphthalene-1,4-dione with aldehydes (Scheme 1).

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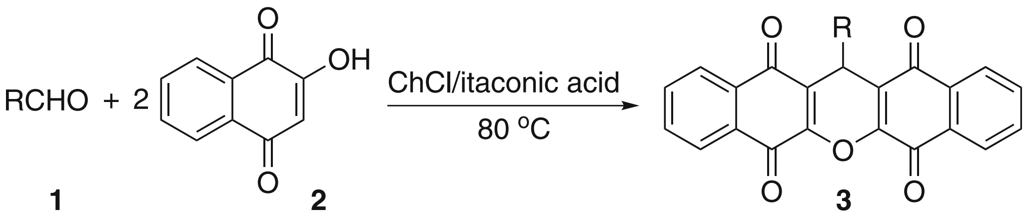
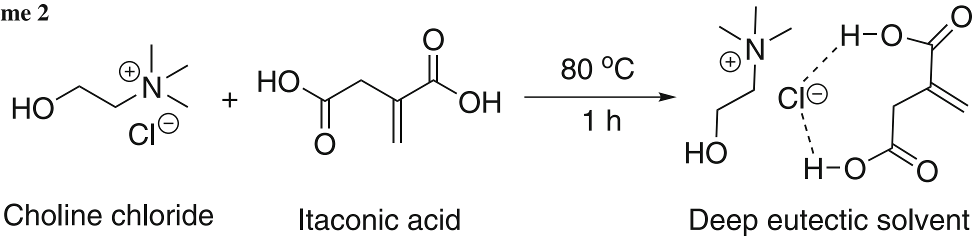
Scheme 1



Scheme 2



Results and discussion

The preparation of ChCl/itaconic acid-based DES was performed by mixing ChCl and itaconic acid at 80 °C until a homogenous colourless liquid was formed (Scheme 2). Then, it was cooled to room temperature and can be directly used without any further purification. This method gave DES with 100 % atom economy since it completely forms a eutectic mixture with no by-product formation.

Figure 1 shows the FT-IR spectra of pure ChCl, itaconic acid versus DES consisting of ChCl and itaconic acid. The characteristic peaks of itaconic acid at 1708, 1438, 1310, 1230, 1218, and 1129 cm^{-1} and peaks of ChCl at 1632, 1478, 1406, 1092, and 949 cm^{-1} can also be observed in the DES. The peaks of OH groups from ChCl and itaconic acid are shifted and broaden due to in the formation of H-bonding in the DES [46].

The thermal stability of ChCl/itaconic acid was investigated by thermogravimetric analysis (TGA) in the N_2 atmosphere, which shows four-stage decomposition, (1) below 162 °C, (2) between 162 and 216 °C, (3) between 216 and 315 °C, and (4) above 350 °C (Fig. 2). The first region, which occurred below 162 °C, displays a mass loss that is attributable to the removal of water. The weight loss of DES appears about 29 % at 162–216 °C which is contributed to the thermal decomposition of ChCl. And a significant mass loss of above 56 % appears between 216 and 315 °C, which may be associated with the thermal decomposition of itaconic acid. Thus, the synthesized DES was stable up to 162 °C, confirming that it could be safely used in organic reactions under 162 °C.

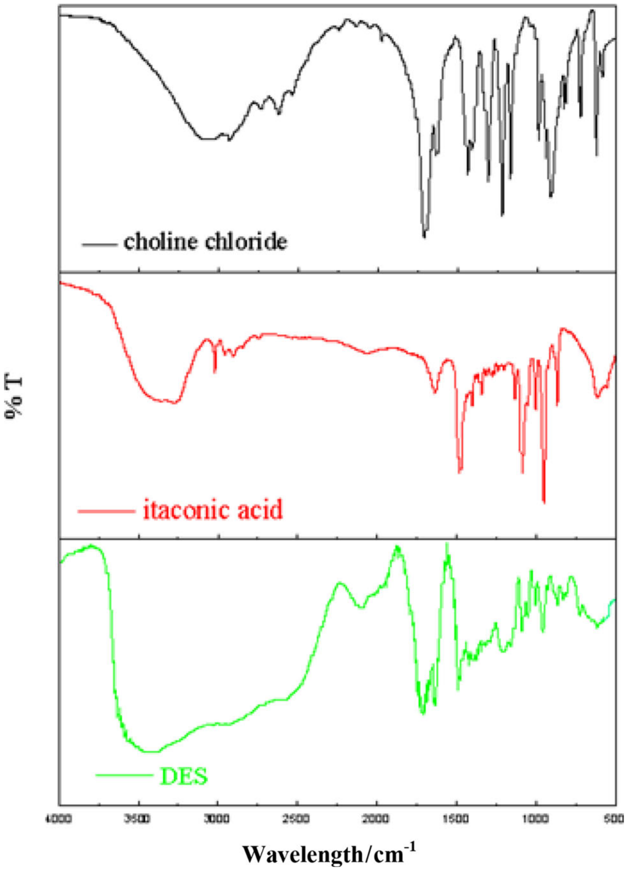


Fig. 1 FTIR spectra of pure ChCl, itaconic acid, and ChCl/itaconic acid

Then, we chose the reaction between 2-hydroxynaphthalene-1,4-dione with benzaldehyde as the prototype to synthesize 13-phenyl-5*H*-dibenzo[*b*,*i*]xanthene-5,7,12,14-

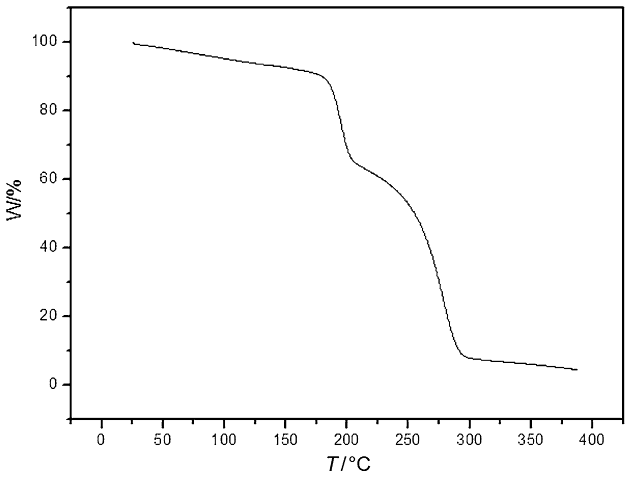


Fig. 2 Thermogravimetric analysis of synthesized ChCl/itaconic acid

(13*H*)-tetraone by using different deep eutectic solvents. As shown in Table 1, no desired product was obtained under solvent-free condition at 100 °C (Table 1, entry 1). Some DESs such as ChCl/ZnCl$_2$, ChCl/FeCl$_3$, ChCl/SnCl$_2$, ChCl/glycerol, ChCl/urea, D-(−)-fructose/DMU, glucose/DMU/NH$_4$Cl were tested and only a trace amount of product was detected (Table 1, entries 2–9). Considering this reaction works well under acidic conditions, some acidic media were investigated in order to obtain satisfactory results. To our great delight, a significant improvement of the yields was observed when the reaction was conducted in DESs such as ChCl/L-(+)-tartaric acid, ChCl/citric acid, ChCl/oxalic acid (entries 10–14). Further study showed that the yield could be increased to as high as 93 % when ChCl/itaconic acid was used (Table 1, entry 18). To optimize the reaction temperature, the model reaction was carried out at different

Table 1 Optimization of the reaction conditions

Entry	DES	Temp/°C	Yield/%[a]
1	No	100	0
2	ChCl/FeCl$_3$ (1:2)	80	Trace
3	ChCl/SnCl$_2$ (1:2)	80	Trace
4	ChCl/ZnCl$_2$ (1:2)	80	Trace
5	ChCl/glycerol (1:2)	80	Trace
6	ChCl/urea (1:2)	80	Trace
7	D-(−)-Fructose/DMU (70:30)[b]	80	Trace
8	Maltose/DMU/NH$_4$Cl (50:40:10)[b]	80	Trace
9	Glucose/DMU/NH$_4$Cl (60:30:10)[b]	80	Trace
10	Citric acid/urea/mannitol (30:20:60)[b]	100	10
11	ChCl/L-(+)-tartaric acid (2:1)	80	35
12	ChCl/citric acid (1:2)	85	43
13	ChCl/oxalic acid (1:1)	88	52
14	ChCl/*p*-TsOH acid (1:1)	80	85
15	ChCl/itaconic acid (1:1)	50	18
16	ChCl/itaconic acid (1:1)	60	34
17	ChCl/itaconic acid (1:1)	70	80
18	ChCl/itaconic acid (1:1)	80	93
19	ChCl/itaconic acid (1:1)	90	93
20	ChCl/itaconic acid (1:1) 0.25 g	80	12
21	ChCl/itaconic acid (1:1) 0.50 g	80	36
22	ChCl/itaconic acid (1:1) 0.75 g	80	81
23	ChCl/itaconic acid (1:1) 1.50 g	80	93
24[c]	ChCl/itaconic acid (1:1)	80	92
25[d]	ChCl/itaconic acid (1:1)	80	92, 90, 89, 87, 85

Reaction conditions: benzaldehyde (1 mmol), 2-hydroxynaphthalene-1,4-dione (2 mmol), solvent (1.0 g), 2 h

[a] Isolated yields

[b] The ratio is given in weight %

[c] The reaction was carried out in 50 mmol scale

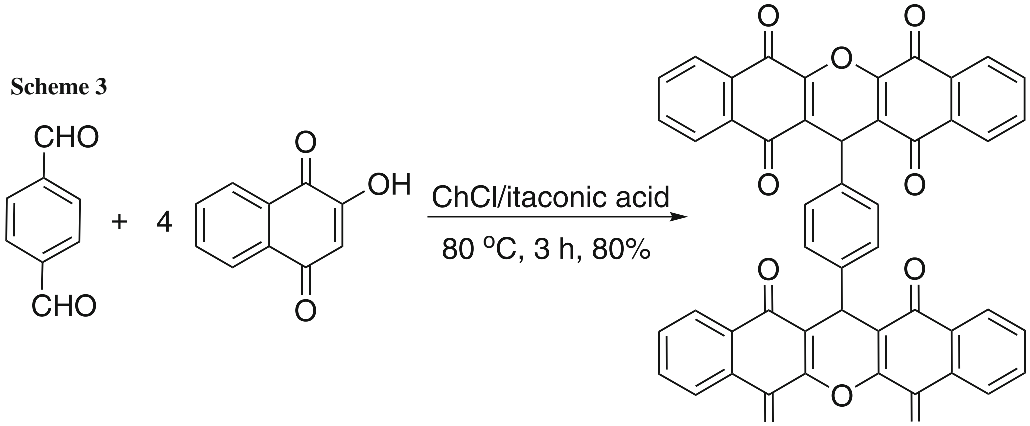
[d] ChCl/itaconic acid was reused for 5 times

Table 2 Synthesis of 13-aryl-5*H*-dibenzo[*b*,*i*]xanthene-5,7,12,14(13*H*)-tetraones in ChCl/itaconic acids

Entry	Aldehyde	Product	Time/h	Yield/%[a]	m.p./°C	
					Found	Reported
1	PhCHO	**3a**	2.0	93	307–308	305–307 [16]
2	4-MeC$_6$H$_4$CHO	**3b**	2.0	91	303–305	304–307 [10]
3	2-HOC$_6$H$_4$CHO	**3c**	2.0	92	218–220	
4	2-MeOC$_6$H$_4$CHO	**3d**	2.0	90	263–264	262–265 [16]
5	4-MeOC$_6$H$_4$CHO	**3e**	2.0	91	>330	>320 [14]
6	3-MeO-4-HOC$_6$H$_3$CHO	**3f**	3.0	89	310–312	
7	3,4-(MeO)$_2$C$_6$H$_3$CHO	**3g**	3.0	88	294–295	>300 [16]
8	3-C$_6$H$_4$OC$_6$H$_4$CHO	**3h**	3.0	92	273–275	
9	4-(CH$_3$)$_3$CC$_6$H$_4$CHO	**3i**	3.0	86	298–300	
10	2-FC$_6$H$_4$CHO	**3j**	1.5	94	271–273	
11	4-FC$_6$H$_4$CHO	**3k**	1.5	90	271–272	270–272 [16]
12	2-BrC$_6$H$_4$CHO	**3l**	1.5	91	284–207	283–285 [16]
13	4-BrC$_6$H$_4$CHO	**3m**	1.5	92	>330	>320 [14]
14	2-ClC$_6$H$_4$CHO	**3n**	1.5	91	306–308	307–309 [10]
15	3-ClC$_6$H$_4$CHO	**3o**	1.5	89	280–282	282–284 [16]
16	4-ClC$_6$H$_4$CHO	**3p**	1.5	90	>330	>320 [14]
17	2-NO$_2$C$_6$H$_4$CHO	**3q**	1.5	91	273–277	
18	3-NO$_2$C$_6$H$_4$CHO	**3r**	1.5	92	>330	340–342 [13]
19	4-NO$_2$C$_6$H$_4$CHO	**3s**	1.5	90	>330	>320 [14]
20	3-Br-5-Cl-2-HOC$_6$H$_2$CHO	**3t**	2.0	88	254–256	
21	2-Thiophenecarbaldehyde	**3u**	3.0	87	263–265	
22	1-Naphthaldehyde	**3v**	3.0	89	319–324	
23	Terephthalaldehyde	**3w**	3.0	89	286–289	

[a] Isolated yield

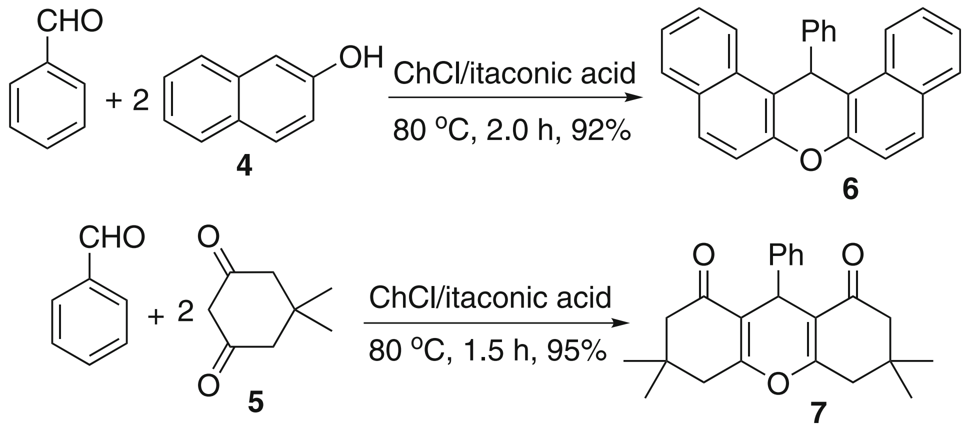
Scheme 3



3x

temperature. It was found that the expected product was obtained from 18 to 93 % yields when the reaction temperature was raised from 50 to 80 °C (Table 1, entries 15–18). However, no increase in the yield of product was observed when the reaction temperature was raised from 80 to 90 °C. By screening different amount of ChCl/itaconic acid, it was found that product was formed in yields ranging from 12 to 93 % (Table 1, entries 19–23). The best amount

Scheme 4



of DES was 1.0 g. Further increase of the DES did not affect the yield (Table 1, entry 23).

In order to demonstrate the practical applicability of this process, the model reaction was carried out in a larger scale (50 mmol of benzaldehyde, 100 mmol of 2-hydroxynaphthalene-1,4-dione in 50 g ChCl/itaconic acid). The reaction was completed in 2 h with 91 % yield (Table 1, entry 24). On the same scale, the recyclability of DES was also explored for the selected model reaction. After completion of the reaction, the mixture was cooled to room temperature and water was added to the reaction mixture. The solid product was isolated by filtration and washed with water. The DES was dissolved in water. The water containing DES was evaporated under reduced pressure and DES was recovered and reused. The recovered DES was reused for five times without a significant reduction in the yield (Table 1, entry 25).

After optimizing the reaction conditions, to test the scope and generality of this protocol, a series of substituted aromatic aldehydes were investigated and the results were summarized in Table 2. Various aromatic aldehydes bearing electron-neutral, electron-rich, or electron-poor groups reacted with 2-hydroxynaphthalene-1,4-dione to afford the desired products in high yields. The product yields were only slightly affected by the location of the substituents (on *ortho*-, *meta*-, or *para*-positions of the benzene ring) (Table 2, entries 2–20). Much to our satisfaction, halo-substituted aldehydes were successfully converted into target products, which allowed for easy further functionalization. Furthermore, the acid-sensitive heterocyclic aldehyde such as 2-thiophenecarbaldehyde was found to be suitable for this transformation and afforded the corresponding product in 87 % yield (Table 2, entry 21). It is noteworthy that the system also worked well for sterically hindered substrate such as 1-naphthaldehyde (Table 2, entry 22). Unfortunately, no product was observed under above conditions when aliphatic aldehydes such as acetaldehyde, *n*-propionaldehyde, 3-methylbutyraldehyde, and cyclohexanecarbaldehyde were used as substrates.

Furthermore, this reaction was further applied for the synthesis of (1,4-phenylene)*bis*(5*H*-dibenzo[*b,i*]xanthene-5,7,12,14(13*H*)-tetraone (**3x**) by the reaction of *p*-phthalaldehyde and 4 equiv. of 2-hydroxynaphthalene-1,4-dione under similar conditions in good yield (Scheme 3). To further expand the potential of this approach as a tool for the construction of xanthenes, we investigated the reaction of benzaldehyde with β-naphthol (**4**) or dimedone (**5**). As shown in Scheme 4, benzaldehyde could react smoothly with β-naphthol or dimedone to give the desired 14-phenyl-14*H*-dibenzo[*a,j*]xanthene (**6**) [27] and 3,3,6,6-tetramethyl-9-phenyl-3,4,5,6,7,9-hexahydro-1*H*-xanthene-1,8(2*H*)-dione (**7**) [47] in high yields.

Conclusion

In summary, the present protocol introduces ChCl/itaconic acid as an efficient catalyst and reaction medium for the synthesis of 13-aryl-5*H*-dibenzo[*b,i*]xanthene-5,7,12,14(13*H*)-tetraones by condensation of 2-hydroxynaphthalene-1,4-dione with various aldehydes. The present protocol offers some advantages such as cleaner reaction profile, metal-free, high yields, simple workup procedure, and avoidance of the use of toxic organic solvents and additional Brønsted or Lewis acid catalysts.

Experimental

All reagents were commercially available and used without further purification. Melting points were determined on an X-4 apparatus. IR spectra were determined on a Thermo

Scientific Nicolet is 50 spectrometer using KBr disks. NMR spectra were recorded at room temperature on a Bruker DRX-500 spectrometer at 500 MHz (^{1}H), 125 MHz (^{13}C) using DMSO-d_6 as the solvent with TMS as internal standard. Mass spectra were operated at a 3200 Qtrap instrument with an ESI source.

DES preparation

Choline chloride (100 mmol) and 100 mmol itaconic acid were mixed in a 250 cm^3 round-bottomed flask. The mixture was heated at 80 °C until a clear liquid appeared. It can be directly used without any further purification.

Typical procedure for preparation of 13-aryl-5*H*-dibenzo[*b,i*]xanthene-5,7,12,14(13*H*)-tetraones

A dry 50 cm^3 flask was charged with aldehyde (1 mmol), 2-hydroxy-1,4-naphthoquinone (2 mmol), and 1.0 g DES and the reaction mixture was stirred at 80 °C. The progress of the reaction was monitored by TLC. After completion of the reaction, the mixture was cooled to room temperature and water was added to the reaction mixture. The solid product was isolated by filtration, washed with water, and purified by recrystallization from ethanol.

Except for compounds **3c**, **3f**, **3h**–**3j**, **3q**, **3t**–**3x**, all products are known compounds. The physical and spectroscopic data for all known compounds were found to be identical to those described in the literature.

13-(2-Hydroxyphenyl)-5H-dibenzo[b,i]xanthene-5,7,12,14(13H)-tetraone (**3c**, $C_{27}H_{14}O_6$)
Brown powder; IR (KBr): $\bar{\nu}$ = 3454, 3053, 1646, 1594, 1575, 1487, 1355, 1243, 1042, 778, 747 cm^{-1}; ^{1}H NMR (DMSO-d_6, 500 MHz): δ = 5.76 (s, 1H), 7.09–7.15 (m, 2H), 7.22–7.28 (m, 2H), 7.75 (t, J = 7.5 Hz, 1H), 7.83 (t, J = 4.5 Hz, 3H), 7.88–7.93 (m, 3H), 7.97–8.07 (m, 2H) ppm; ^{13}C NMR (DMSO-d_6, 125 MHz): δ = 116.3, 125.3, 125.5, 125.6, 125.8, 128.3, 128.6, 129.9, 130.2, 131.1, 131.6, 133.0, 133.7, 134.5, 134.6, 148.7, 151.2, 177.8, 182.8 ppm; MS (ESI): m/z = 435 ([M + 1]$^+$).

13-(4-Hydroxy-3-methoxyphenyl)-5H-dibenzo[b,i]xanthene-5,7,12,14(13H)-tetraone (**3f**, $C_{28}H_{16}O_7$)
Dark red solid; IR (KBr): $\bar{\nu}$ = 3480, 2972, 1661, 1607, 1514, 1452, 1275, 1192, 1152, 769, 722 cm^{-1}; ^{1}H NMR (DMSO-d_6, 500 MHz): δ = 3.64 (s, 3H), 3.74 (s, 1H), 5.96 (s, 1H), 6.58 (s, 2H), 6.79 (s, 1H), 7.77 (dd, J = 1.0 Hz, 7.0 Hz, 2H), 7.80–7.83 (m, 2H), 7.94 (t, J = 7.0 Hz, 2H), 7.98 (dd, J = 1.0 Hz, 7.0 Hz, 2H) ppm; ^{13}C NMR (DMSO-d_6, 125 MHz): δ = 32.9, 56.2, 113.9, 115.7, 116.0, 121.9, 123.9, 124.6, 126.5, 126.6, 129.2, 130.0, 130.8, 131.2, 131.7, 132.1, 132.8, 134.8, 135.2, 135.7, 146.4, 147.7, 149.0, 155.3, 177.3, 177.5, 178.4, 183.3 ppm; MS (ESI): m/z = 465 ([M + 1]$^+$).

13-(3-Phenoxyphenyl)-5H-dibenzo[b,i]xanthene-5,7,12,14(13H)-tetraone (**3h**, $C_{33}H_{18}O_6$)
Red solid; IR (KBr): $\bar{\nu}$ = 3451, 2979, 1637, 1482, 1285, 1153, 1093, 1047, 742, 659 cm^{-1}; ^{1}H NMR (DMSO-d_6, 500 MHz): δ = 6.69 (d, J = 6.5 Hz, 2H), 6.81 (s, 1H), 6.91 (d, J = 8.0 Hz, 3H), 7.00 (t, J = 7.0 Hz, 1H), 7.17 (t, J = 8.0 Hz, 1H), 7.26 (t, J = 8.0 Hz, 2H), 7.66 (t, J = 7.5 Hz, 2H), 7.75 (t, J = 7.0 Hz, 2H), 7.87 (d, J = 7.5 Hz, 2H), 7.95 (d, J = 7.5 Hz, 2H) ppm; ^{13}C NMR (DMSO-d_6, 125 MHz): δ = 32.9, 115.0, 117.5, 117.8, 122.1, 122.7, 125.0, 125.6, 129.0, 129.6, 130.8, 131.7, 133.1, 133.6, 143.8, 155.8, 156.7, 183.4 ppm; MS (ESI): m/z = 511 ([M + 1]$^+$).

13-[4-(tert-Butyl)phenyl]-5H-dibenzo[b,i]xanthene-5,7,12,14(13H)-tetraone (**3i**, $C_{31}H_{22}O_5$)
Orange solid; IR (KBr): $\bar{\nu}$ = 3420, 2963, 2867, 1681, 1664, 1592, 1456, 1358, 1091, 1049, 720, 665 cm^{-1}; ^{1}H NMR (DMSO-d_6, 500 MHz): δ = 1.19 (s, 9H), 5.10 (s, 1H), 7.28 (d, J = 9.5 Hz, 2H), 7.36 (d, J = 9.0 Hz, 2H), 7.73 (s, 1H), 7.87–7.90 (m, 2H), 7.94–7.97 (m, 2H), 8.01 (d, J = 7.5 Hz, 1H), 8.11–8.13 (m, 2H) ppm; ^{13}C NMR (DMSO-d_6, 125 MHz): δ = 31.5, 32.9, 34.6, 115.9, 123.9, 124.6, 124.9, 126.2, 126.5, 126.7, 127.0, 129.2, 130.9, 131.2, 131.4, 131.6, 132.2, 132.3, 134.9, 135.2, 138.9, 149.2, 149.9, 155.6, 177.2, 177.4, 178.3, 183.2 ppm; MS (ESI): m/z = 475 ([M + 1]$^+$).

13-(2-Fluorophenyl)-5H-dibenzo[b,i]xanthene-5,7,12,14(13H)-tetraone (**3j**, $C_{27}H_{13}FO_5$)
Red powder; IR (KBr): $\bar{\nu}$ = 3447, 2971, 1640, 1485, 1371, 1279, 1224, 1151, 1050, 744, 730 cm^{-1}; ^{1}H NMR (DMSO-d_6, 500 MHz): δ = 6.72 (s, 1H), 7.02–6.94 (m, 2H), 7.16–7.12 (m, 1H), 7.24 (t, J = 7.5 Hz, 1H), 7.67 (t, J = 7.5 Hz, 2H), 7.75 (t, J = 7.5 Hz, 2H), 7.88 (d, J = 7.5 Hz, 2H), 7.95 (d, J = 7.5 Hz, 2H) ppm; ^{13}C NMR (DMSO-d_6, 125 MHz): δ = 28.7, 114.7 (d, $^{2}J_{CF}$ = 22 Hz), 122.3 (d, $^{1}J_{CF}$ = 224.2 Hz), 125.0, 125.6, 126.9 (d, $^{3}J_{CF}$ = 8.1 Hz), 128.6, 128.7, 130.7 (d, $^{4}J_{CF}$ = 3.8 Hz), 130.8, 131.9, 133.0, 133.7, 159.4, 161.3, 164.3, 181.9, 183.5 ppm; MS (ESI): m/z = 437 ([M + 1]$^+$).

13-(2-Nitrophenyl)-5H-dibenzo[b,i]xanthene-5,7,12,14(13H)-tetraone (**3q**, $C_{27}H_{13}NO_7$)
Yellow solid; IR (KBr): $\bar{\nu}$ = 3449, 2983, 1659, 1637, 1556, 1438, 1326, 1265, 1090, 1043, 792, 745 cm^{-1}; ^{1}H NMR (DMSO-d_6, 500 MHz): δ = 6.18 (s, 1H), 7.42–7.46 (m, 1H), 7.53–7.56 (m, 1H), 7.68 (dd, J = 1.5 Hz, 8 Hz, 2H), 7.67–7.69 (m, 1H), 7.89–7.90 (m, 1H), 7.913–7.93 (m, 2H), 7.98–7.99 (m, 1H), 8.00–8.04 (m, 2H), 8.12–8.15 (m, 1H) ppm; ^{13}C NMR (DMSO-d_6, 125 MHz): δ = 33.5,

120.7, 121.9, 122.6, 125.7, 126.3, 129.8, 131.5, 132.5, 134.4, 135.6, 144.7, 148.3, 165.2, 182.8, 183.9 ppm; MS (ESI): $m/z = 464$ ($[M + 1]^+$).

13-(3-Bromo-5-chloro-2-hydroxyphenyl)-5H-dibenzo[b,i]xanthene-5,7,12,14(13H)-tetraone (**3t**, $C_{27}H_{14}BrClO_6$)
Yellow solid; IR (KBr): $\bar{\nu} = 3445, 2996, 2842, 1657, 1637, 1580, 1486, 1282, 1255, 1092, 845, 725\ cm^{-1}$; ^1H NMR (DMSO-d_6, 500 MHz): $\delta = 5.74$ (s, 1H), 7.12 (s, 1H), 7.69 (d, $J = 7.5$ Hz, 1H), 7.73 (t, $J = 8.5$ Hz, 2H), 7.86–7.88 (m, 2H), 7.89–7.90 (m, 2H), 7.91 (d, $J = 9.0$ Hz, 2H), 8.05 (t, 1H) ppm; ^{13}C NMR (DMSO-d_6, 125 MHz): $\delta = 28.8$, 111.4, 122.5, 126.5, 128.2, 129.5, 130.7, 131.6, 132.5, 134.6, 135.2, 145.5, 147.4, 151.1, 151.2, 177.7, 182.5, 183.1 ppm; MS (ESI): $m/z = 546$ ($[M + 1]^+$).

13-(Thiophen-2-yl)-5H-dibenzo[b,i]xanthene-5,7,12,14(13H)-tetraone (**3u**, $C_{25}H_{12}O_5S$)
Dark green solid; IR (KBr): $\bar{\nu} = 3420, 2973, 1684, 1663, 1576, 1355, 1290, 1049, 1008, 757, 714\ cm^{-1}$; ^1H NMR (DMSO-d_6, 500 MHz): $\delta = 5.40$ (s, 1H), 6.86–6.88 (m, 1H) 7.08 (d, $J = 3.0$ Hz, 1H), 7.37 (dd, $J = 1.0$ Hz, 5.0 Hz, 1H), 7.75 (t, $J = 7.0$ Hz, 1H), 7.91–7.93 (m, 2H), 7.95–7.98 (m, 1H), 8.03–8.06 (m, 2H), 8.09 (d, $J = 7.0$ Hz, 1H), 8.13–8.15 (m, 1H) ppm; ^{13}C NMR (DMSO-d_6, 125 MHz): $\delta = 27.6$, 115.3, 123.1, 124.7, 126.4, 126.5, 126.7, 127.3, 129.3, 129.7, 130.9, 131.2, 131.5, 132.3, 135.0, 135.3, 135.7, 144.2, 149.2, 155.8, 177.3, 178.1, 183.0 ppm; MS (ESI): $m/z = 425$ ($[M + 1]^+$).

13-(Naphthalen-1-yl)-5H-dibenzo[b,i]xanthene-5,7,12,14(13H)-tetraone (**3v**, $C_{31}H_{16}O_5$)
Orange solid; IR (KBr): $\bar{\nu} = 3445, 2976, 1675, 1661, 1590, 1352, 1286, 1192, 1048, 942, 777\ cm^{-1}$; ^1H NMR (DMSO-d_6, 500 MHz): $\delta = 6.31$ (s, 1H), 7.46 (t, $J = 7.0$ Hz, 1H), 7.73 (t, $J = 7.5$ Hz, 2H), 7.84–7.88 (m, 4H), 7.94–7.97 (m, 5H), 8.08–8.10 (m, 1H), 8.23 (d, $J = 8.5$ Hz, 2H) ppm; ^{13}C NMR (DMSO-d_6, 125 MHz): $\delta = 32.5$, 123.4, 124.8, 125.3, 125.5, 125.6, 125.7, 126.3, 126.4, 126.6, 129.0, 131.9, 132.5, 133.6, 134.2, 134.4, 137.8, 183.9 ppm; MS (ESI): $m/z = 469$ ($[M + 1]^+$).

4-(5,7,12,14-Tetraoxo-7,12,13,14-tetrahydro-5H-dibenzo[b,i]xanthen-13-yl)benzaldehyde (**3w**, $C_{28}H_{14}O_6$)
Dark red solid; IR (KBr): $\bar{\nu} = 3445, 2976, 1681, 1607, 1577, 1487, 1229, 1195, 1152, 773, 718, 646\ cm^{-1}$; ^1H NMR (DMSO-d_6, 500 MHz): $\delta = 5.21$ (s, 1H), 7.71–7.76 (m, 4H), 7.81 (d, $J = 8.5$ Hz, 2H), 7.88–7.91 (m, 4H), 8.11–8.14 (m, 2H), 9.93 (s, 1H) ppm; ^{13}C NMR (DMSO-d_6, 125 MHz): $\delta = 34.1$, 115.0, 122.8, 124.8, 126.5, 129.2, 129.9, 130.6, 131.0, 131.2, 131.6, 132.3, 134.9, 135.2, 135.5, 135.6, 148.4, 149.6, 155.7, 177.1, 177.4, 178.1, 183.2 ppm; MS (ESI): $m/z = 447$ ($[M + 1]^+$).

13,13'-(1,4-Phenylene)bis(5H-dibenzo[b,i]xanthene-5,7,12,14(13H)-tetraone) (**3x**, $C_{48}H_{22}O_{10}$)
Dark red solid; m.p.: 323–326 °C; IR (KBr): $\bar{\nu} = 3446, 2973, 1661, 1607, 1515, 1456, 1276, 1193, 1153, 769, 722, 625\ cm^{-1}$; ^1H NMR (DMSO-d_6, 500 MHz): $\delta = 5.10$ (d, $J = 6.0$ Hz, 1H), 5.22 (s, 1H), 7.03 (d, $J = 8.5$ Hz, 1H), 7.24 (d, $J = 8.5$ Hz, 1H), 7.34 (t, $J = 6.5$ Hz, 1H), 7.68–7.77 (m, 8H), 7.81 (d, $J = 8.5$ Hz, 1H), 7.88–7.92 (m, 8H), 7.95 (t, $J = 4.0$ Hz, 2H), 7.99 (d, $J = 8.5$ Hz, 1H), 8.14 (t, $J = 6.5$ Hz, 2H) ppm; ^{13}C NMR (DMSO-d_6, 125 MHz): $\delta = 34.1$, 115.0, 122.8, 124.8, 126.5, 126.7, 129.2, 129.7, 130.6, 130.7, 131.0, 131.2, 131.6, 132.3, 134.9, 135.2, 135.5, 135.6, 149.6, 155.7, 177.1, 177.4, 178.1, 183.2 ppm; MS (ESI): $m/z = 759$ ($[M + 1]^+$).

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