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Synthesis and antioxidant studies of novel bi-, tri-, and tetrapodal 9-aryl-1,8-dioxo-octahydroxanthenes

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ABSTRACT

Compounds bearing two, three, and four 9-aryl-1,8-dioxo-octahydroxanthenes units were synthesized by regioselective O-alkylation of monopodal xanthenes with bis-, tris-, and tetrakis(bromomethyl)benzenes as alkylating agents using K_2CO_3 as base and DMF as solvent in moderate temperature. All the synthesized compounds were characterized by NMR and mass spectral data and then tested for antioxidant activity, as reflected by free radical scavenging, increased with increasing number of xanthene units.

Xanthenes are common natural products and an important motif in a variety of biologically active and useful compounds.[1] Compounds carrying the xanthene moiety exhibit promising biological activities, such as anticancer,[2] analgesic,[3] anti-inflammatory,[4] and antibacterial[5] activities. In addition, xanthene derivatives can be used as pH sensitive fluorescent materials for the visualization of bio-molecular assemblies,[6] as bactericides in agriculture[7] and in laser technologies.[8] Some of the xanthene based compounds have found applications as antagonists of zoxalamine and in photodynamic therapy.[9] In particular, naphtha-pyranopyrimidines have been reported to be antagonists for the neuropeptide S receptor (NPSR)[10] that is a novel drug target for the treatment of respiratory, sleep, anxiety, and addiction disorders.[11]

Organic compounds like dendrimers containing repeating structural motifs have found application in macromolecular chemistry, by light harvesting,[12] by photodynamic therapy,[13] as dyes,[14] as catalysts,[15] for molecular encapsulation,[16] for multivalent diagnostics by magnetic resonance imaging[17] and for blood substitution.[18] Moreover, the tripodal derivative of 1,3,5-tris(*N*-alkylaminomethyl)benzene has drawn much attention as an efficient building block for the synthesis of functional moieties such as molecular receptors, since its aryl ring acts as a tiny inflexible platform for receptor synthesis.[19] Similarly the bipodal and tetrapodal moieties of trimethyne thiacarbocyanine dyes and fluoromethyl pyrroles (FMPs) have found applications in energy storage systems.[20] The conjugated chromophores of bis- and tris(indolyl)methanes are used as pH indicators and calorimetric chemosensors for transition metals.[21]

So far, mostly monopodal xanthenes have been studied while reports on polypodal xanthenes are rare. According to the factors mentioned and our continuous interest in synthesis of bi-, tri-, and tetrapodal organic compounds,[22] we report herein the first successful synthesis of bi-, tri-, and tetrapodal 9-aryl-1,8-dioxo-octahydroxanthenes and its antioxidant properties.

The basic building block 9-aryl-1,8-dioxo-octahydroxanthenes **5**, **6,** and **7**[23] were synthesized through condensation reaction of dimedone (**4**) and hydroxy benzaldehydes (**1**–**3**) using ethanol as solvent in the presence of catalytic amount of BF_3/OEt_2[24] (Table 1) (Scheme 1).

The synthetic pathways leading to bipodal, tripodal, and tetrapodal xanthenes using **5**, **6,** and **7** are outlined in Schemes 2–4 respectively. Synthesis of compounds **14**–**28** was achieved by regioselective O-alkylation of 9-aryl-1,8-dioxo-octahydroxanthenes **5**, **6,** and **7** with bis-, tris-, and tetrakis(bromomethyl)benzenes **8**–**13**

Table 1
Synthesis of monopodal xanthenes

Product	R_1	R_2	R_3	Time (h)	*T* (°C)	Yield (%)
5	–H	–OH	–H	4	50	92
6	$–OCH_3$	–OH	$–OCH_3$	3	50	93
7	–H	$–OCH_3$	–OH	3	50	93

Dimedone (2.1 mmol), benzaldehydes (1 mmol), BF_3/OEt_2 (10 mol %) in ethanol at 50 °C.

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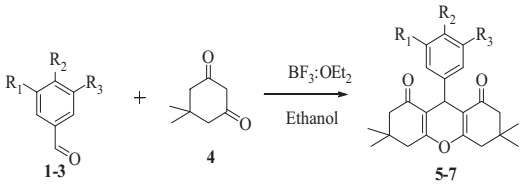


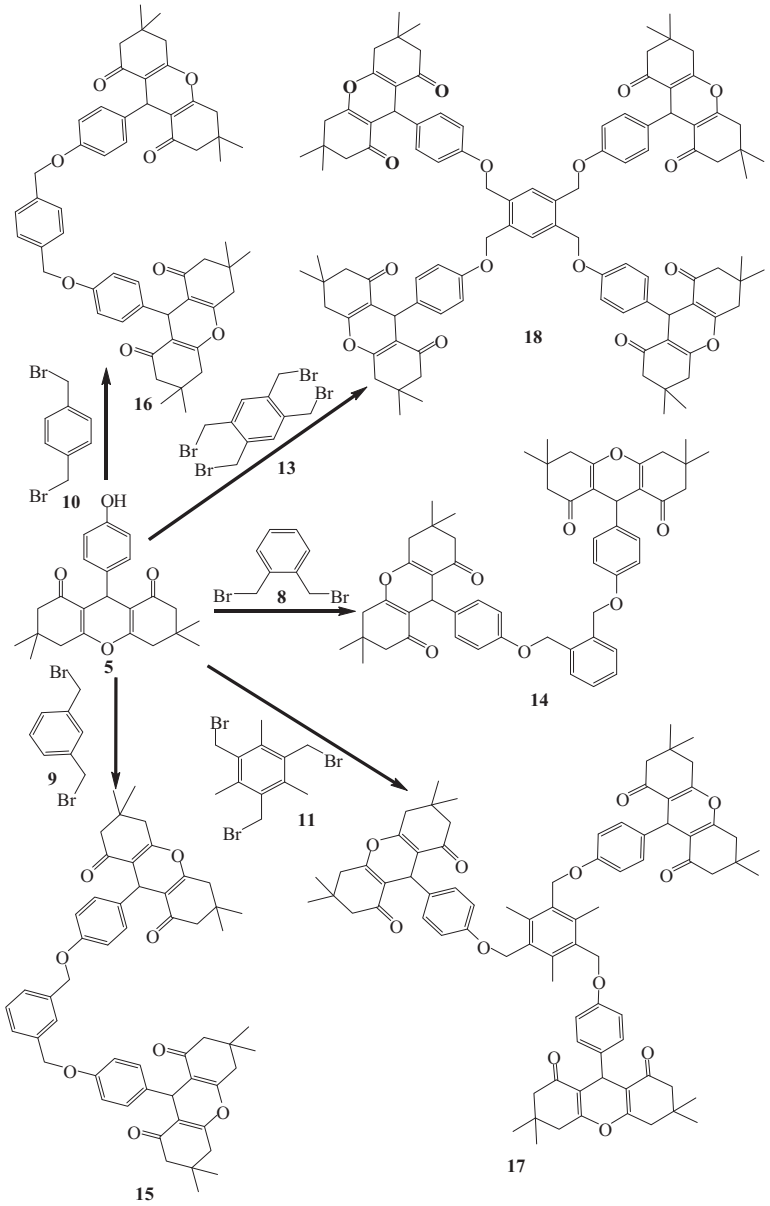
Scheme 1. Synthesis of monopodal xanthenes.

as alkylating agents in the presence of K_2CO_3 in DMF under stirring for 48 h at 70 °C.[28]

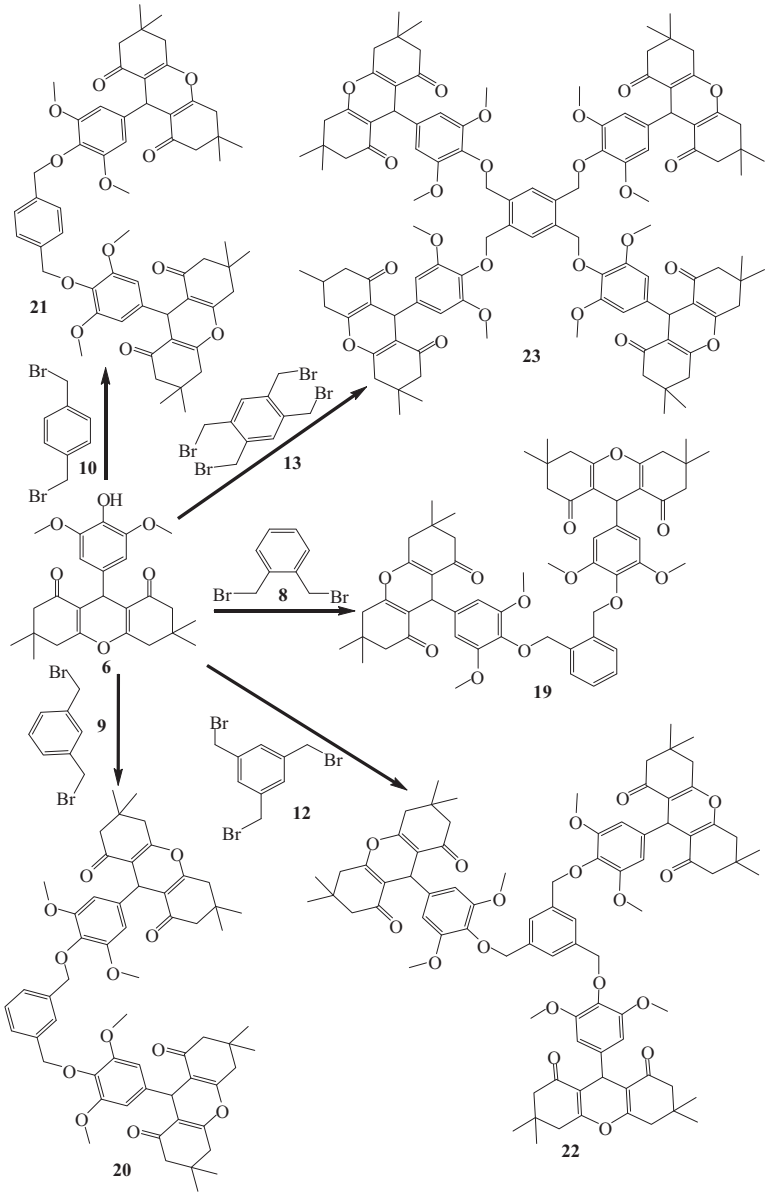
Initially, the reaction was attempted with different bases like K_2CO_3, KOH, *t*-BuOK, and Et_3N to increase the yield of the product. The reaction was found to be good with K_2CO_3, a mild base which afforded the desired product in a high yield. Different solvents such as DMF, DMSO, THF, and acetonitrile were also examined and it was observed that the yields were better with DMF and hence, DMF was considered as a suitable solvent (Table 2).

Bipodal derivatives of xanthenes were synthesized through the reaction of 1 equiv of different bis(bromomethyl)benzenes **8**, **9,** and **10** with 2 equiv of xanthenes **5**, **6,** and **7** in the presence of K_2CO_3 in DMF under stirring for 48 h at 70 °C (Table 3). The ^1H NMR spectrum of bipodal derivative **16**[29] showed two singlets at δ 0.99 and δ 1.09 for 24 methyl protons, a sharp singlet at δ 4.96 for 4 *O*-methylene protons, a sharp singlet at δ 4.69 for 2 methine protons in addition to the aromatic protons. The ^{13}C NMR spectrum of compound **16** displayed three peaks at δ 40.89, δ 69.69, and δ 196.53 for methine, *O*-methylene, and carbonyl carbons in addition to olefinic and aromatic carbons. The *m*/*z* value observed at 835.4199 in the HRMS spectrum also confirmed the formation of the bipodal derivative **16**.

A similar synthetic strategy was adopted to synthesize the trimers by the reaction of 1 equiv of 1,3,5-tris(bromomethyl) benzenes (**11**, **12**) with 3 equiv of xanthenes **5**, **6,** and **7** in presence



Scheme 2. Synthesis of bi-, tri-, and tetrapodal derivatives of xanthene **5**.



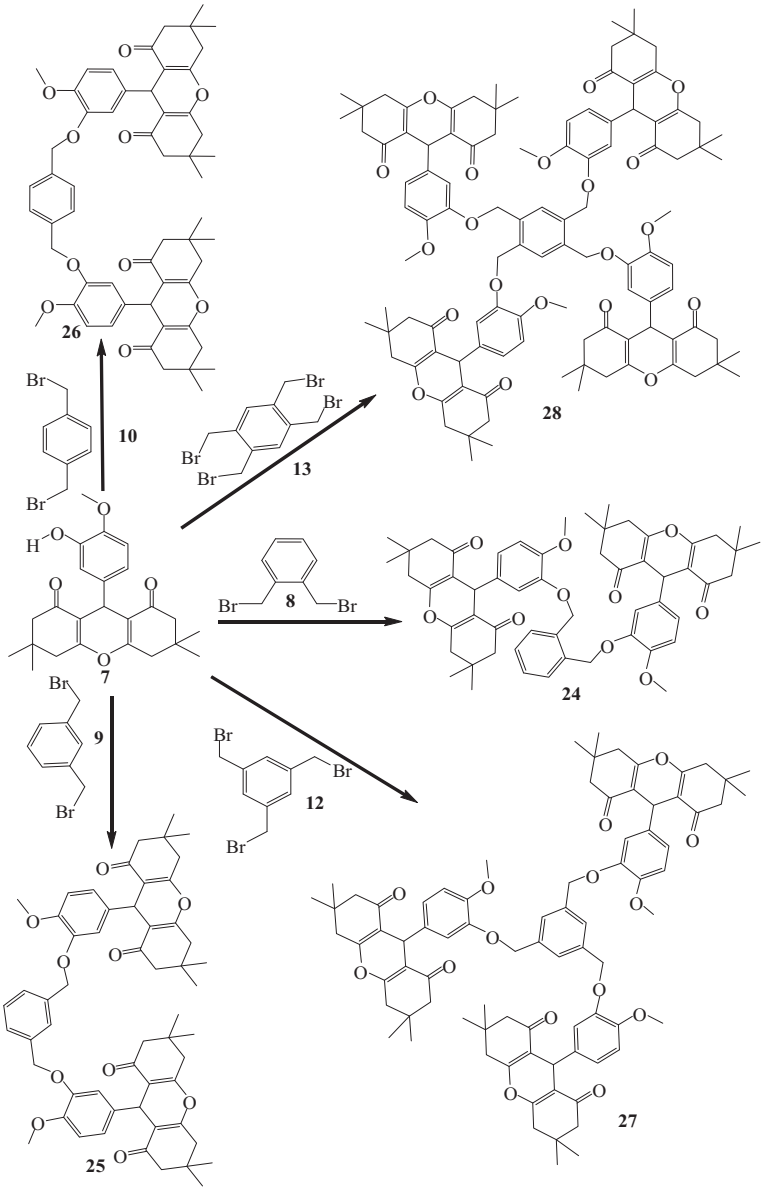
Scheme 3. Synthesis of bi-, tri-, and tetrapodal derivatives of xanthene **6**.

of K_2CO_3 in DMF (Table 3). The ^{1}H NMR spectrum of the tripodal derivative **22**[30] showed two singlets at δ 1.01 and δ 1.10 integrating for 36 methyl protons, a broad singlet at δ 3.77 for 18 methoxy protons, a sharp singlet at δ 4.72 for 3 methine protons, a sharp singlet at δ 4.90 for 6 *O*-methylene protons in addition to aromatic protons. The ^{13}C NMR spectrum of compound **23** displayed four peaks at δ 40.92, δ 56.21, δ 74.94, and δ 196.49 for methine, methoxy, *O*-methylene and carbonyl carbons in addition to olefinic and aromatic carbons. The *m*/*z* value observed at 1393.6500 in the HR-MS spectrum also confirmed the formation of the trimer.

Likewise the tetramers of xanthenes were synthesized from the reaction of 1 equiv of 1,2,4,5-tetrakis(bromomethyl)benzene (**13**) with 4 equiv of building blocks **5**, **6,** and **7** under the same reaction conditions (Table 3). The ^{1}H NMR spectrum of tetrapodal derivative **18**[31] showed two singlet peaks at δ 0.99 and δ 1.09 for 48 methyl group protons, a sharp singlet at δ 5.02 for eight *O*-methylene protons, a sharp singlet at δ 4.69 for four methine protons in addition to the aromatic protons. The ^{13}C NMR spectrum of compound **16** displayed three peaks at δ 40.87, δ 67.43, and δ 196.56 for methine, *O*-methylene, and carbonyl carbons in addition to olefinic and aromatic carbons. The *m*/*z* value observed at 1631 $[M+K]^+$ in the MALDI-TOF mass spectrum also confirmed the formation of the target molecule.

Antioxidant activity

Radical scavenging activity is very important due to the deleterious role of free radicals in foods and in biological systems. The antioxidant activity of the synthesized compounds was investigated using DPPH (2,2-diphenyl-1-picrylhydrazyl) free radical scavenging assay with respect to the standard BHT (butylated hydroxy toluene) using the literature method.[25] All compounds **14**–**28** were dissolved in DMSO with concentration of 10, 50, 100, 250, 500, and 1000 μg/ml then mixed with freshly prepared 2 ml of 0.1 mM DPPH solution and left in dark for 30 min.



Scheme 4. Synthesis of bi-, tri-, and tetrapodal derivatives of xanthene **7**.

Table 2
Synthesis of bipodal derivative **16** in different conditions

Entry	Base	Solvent	Time (h)	*T* (°C)	Yield (%)
1	K_2CO_3	DMF	48	70	81
2	KOH	DMF	48	70	37
4	*t*-BuOK	DMF	48	70	12
5	Et_3N	DMF	48	70	44
6	K_2CO_3	DMSO	48	70	67
7	K_2CO_3	THF	48	70	8
8	K_2CO_3	acetonitrile	48	70	19
9	K_2CO_3	DMF	36	70	38
10	K_2CO_3	DMF	60	70	81
11	K_2CO_3	DMF	48	RT	6
12	K_2CO_3	DMF	48	90	72

1,4-Bis(bromomethyl)benzene **10** (1 mmol), xanthene **5** (2 mmol) under the above conditions.

Subsequently, the absorbance was measured at 517 nm and the observed values are given in Table 4. Percentage activity of the compounds was calculated using the following equation.

$$\text{Inhibition}(\%) = [1 - (A_{\text{sample}}/A_{\text{control}})] \times 100$$

where A_{control} is the absorbance of the control (blank, without compound) and A_{sample} is the absorbance of the compounds. The percentage of inhibition is shown in Figure 1 which reveals the radical scavenging activity of xanthenes on DPPH radicals increases with increase in concentration. Moreover, the activity of xanthenes gradually increases from dimers to trimers, which could be due to the more number of xanthene units in the trimers, generally termed as multivalent effect.[26] Based on the similar trend, tetramers should show much greater antioxidant property.

However, trimers and tetramers showed more or less the same activity due to crowding effect which causes serious steric hindrance and decrease the availability of xanthene units to exhibit antioxidant property.[27]

Among all the compounds, the tripodal derivative (**22**) of xanthene **6** showed maximum activity at a concentration of 1000 μg/ml.

In conclusion, the monopodal xanthenes served as building blocks for the construction of novel bi-, tri-, and tetrapodal

Table 3
Synthesis of xanthenes using various alkylating agents

Entry	Alkylating agent	Xanthenes	Product	Yield[a] (%)
1	1,4-Bis(bromomethyl)benzene **10**	5	16	81
2	1,3-Bis(bromomethyl)benzene **9**	5	15	75
3	1,2-Bis(bromomethyl)benzene **8**	5	14	77
4	1,4-Bis(bromomethyl)benzene **10**	6	21	83
5	1,3-Bis(bromomethyl)benzene **9**	6	20	85
6	1,2-Bis(bromomethyl)benzene **8**	6	19	80
7	1,4-Bis(bromomethyl)benzene **10**	7	26	81
8	1,3-Bis(bromomethyl)benzene **9**	7	25	75
9	1,2-Bis(bromomethyl)benzene **8**	7	24	74
10	2,4,6-Tris(bromomethyl)mesitylene **11**	5	17	63
11	1,3,5-Tris(bromomethyl)benzene **12**	6	22	71
12	1,3,5-Tris(bromomethyl)benzene **12**	7	27	62
13	1,2,4,5-Tetrakis(bromomethyl)benzene **13**	5	18	58
14	1,2,4,5-Tetrakis(bromomethyl)benzene **13**	6	23	62
15	1,2,4,5-Tetrakis(bromomethyl)benzene **13**	7	28	56

[a] The yields refer to the isolated pure products.

Table 4
Antioxidant activity for the compounds **14**–**28** by DPPH method

S. no.	Concentration											
	10 μg/ml		50 μg/ml		100 μg/ml		250 μg/ml		500 μg/ml		1000 μg/ml	
	A	I	A	I	A	I	A	I	A	I	A	I
BHT	0.212	77	0.066	93	0.055	94	0.046	95	0.039	96	0.016	98
14	0.848	8	0.755	18	0.636	31	0.571	38	0.541	41	0.534	42
15	0.847	8	0.764	17	0.626	32	0.589	36	0.488	47	0.461	50
16	0.829	10	0.737	20	0.598	35	0.525	43	0.497	46	0.442	52
17	0.81	12	0.672	27	0.543	41	0.267	71	0.211	77	0.175	81
18	0.801	13	0.635	31	0.525	43	0.258	72	0.193	79	0.165	82
19	0.830	10	0.727	21	0.598	35	0.545	41	0.497	46	0.451	51
20	0.821	11	0.709	23	0.595	35	0.552	40	0.506	45	0.423	54
21	0.801	13	0.711	23	0.58	37	0.516	44	0.442	52	0.413	55
22	0.792	14	0.635	31	0.543	41	0.322	65	0.193	79	0.147	84
23	0.792	14	0.645	30	0.562	39	0.35	62	0.211	77	0.193	79
24	0.856	7	0.726	21	0.635	31	0.534	42	0.535	42	0.497	46
25	0.830	10	0.718	22	0.608	34	0.516	44	0.453	51	0.442	52
26	0.82	11	0.727	21	0.582	37	0.517	44	0.442	52	0.414	55
27	0.791	14	0.654	29	0.506	45	0.258	72	0.221	76	0.156	83
28	0.783	15	0.626	32	0.516	44	0.248	73	0.211	77	0.175	81
Control	0.9215											

A—absorbance I—inhibition percentage.

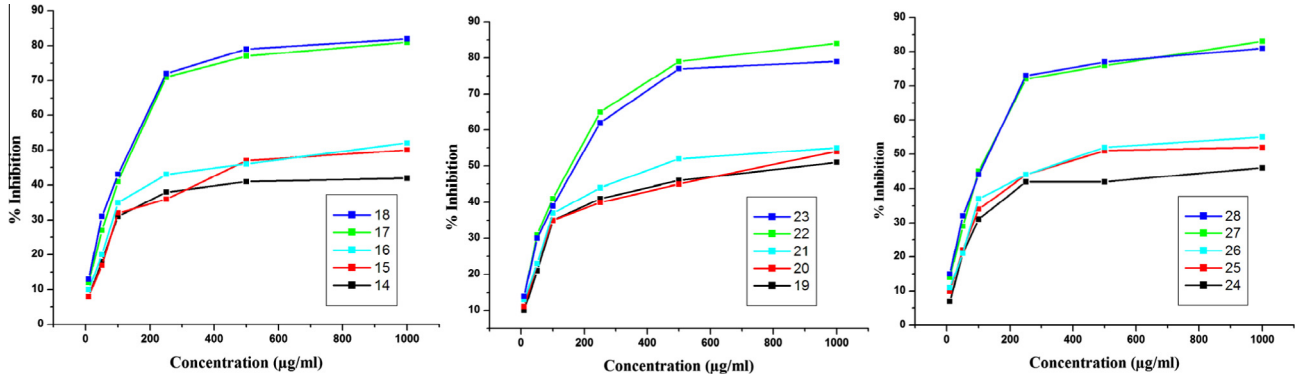


Figure 1. DPPH radical scavenging activity of various concentrations of the bi-, tri-, and tetrapodal compounds (**14**–**28**) of xanthenes **5**, **6,** and **7**.

xanthenes by conventional methodology. The antioxidant activity of the synthesized compounds was also studied and it showed that the efficiency is concentration dependent as well as it depends on the size of the compounds.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2015.01.162.

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28. *General procedure for synthesis of bi-, tri-, and tetrapodal xanthenes* (**14**–**28**): To a solution of 1 equiv of xanthenes **5**, **6,** and **7** in 5 ml of dry DMF, 2 equiv of powdered K_2CO_3 was added, stirred well for 30 min at room temperature. To that, alkylating agent (0.5 equiv in case of dimers; 0.333 equiv in case of trimers; 0.25 equiv in case of tetramers dissolved in minimum amount of DMF was added drop wise for 1 h with stirring at 50 °C. After the complete addition, the reaction mixture was stirred at 70 °C for 48 h. After completion of the reaction as indicated by TLC, the reaction mixture was poured into a beaker containing ice cold water and stirred well. The precipitate was collected and, if necessary, purified by column chromatography on silica gel (60–120 mesh). (The bipodal derivatives were purified using hexane/ethylacetate (75:25) solvent mixture whereas tripodal and tetrapodal derivatives were purified using the chloroform/methanol (99.7:0.3) solvent mixture as eluent).
29. *Bipodal derivative: 9,9′-(4,4′-(1,4-phenylenebis(methylene)) bis(oxy)bis(4,1-phenylene))bis (3,3,6,6-tetramethyl-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione)* (**16**): White solid; mp 236–237 °C; ^{1}H NMR (400 Hz, $CDCl_3$) δ 0.99, 1.09 (s, 24H, CH_3), 2.21 (q, J = 9.2 Hz, 8H, CH_2), 2.45 (s, 8H, CH_2), 4.69 (s, 2H, CH), 4.96 (s, 4H, CH_2), 6.81 (d, J = 8 Hz, 4H, ArH), 7.21 (d, J = 8.0 Hz, 4H, ArH), 7.38 (m, 4H, ArH); ^{13}C NMR (100 Hz, $CDCl_3$) δ 27.41, 29.28, 30.99, 32.23, 40.89, 50.80, 69.69, 114.36, 115.18, 115.80, 127.74, 129.37, 136.80, 136.90, 157.29, 162.11, 196.53. DEPT-135 (100 MHz, $CDCl_3$): δ 27.41 (CH_3, C-11, 11′), 29.27 (CH_3, C-12, 12′), 30.98 (CH, C-4), 40.88 (CH_2, C-7, 7′), 50.79 (CH_2, C-9, 9′), 69.69 (CH_2, C-17), 114.36 (CH, C-15, 15′), 127.74 (CH, C-19, 19′, 20, 20′), 129.37 (CH, C-14, 14′) ppm; HRMS (m/z): calcd 835.4210 (M+). Found: 835.4199.
30. *Tripodal derivative: 9,9′,9″-(4,4′,4″-(benzene-1,3,5-triyltris(methylene))tris(oxy) tris(3,5-dimethoxybenzene-4,1-diyl))tris(3,3,6,6-tetramethyl-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione)* (**22**): White solid; mp 140–142 °C; ^{1}H NMR (400 Hz, $CDCl_3$) δ 1.01, 1.10 (s, 36H, CH_3), 2.22 (s, 12H, CH_2), 2.46 (s, 12H, CH_2), 3.77 (s, 18H, OCH_3), 4.72 (s, 3H, CH), 4.90 (s, 6H, CH_2), 6.50 (s, 6H, ArH), 7.53 (s, 3H, ArH); ^{13}C NMR (100 Hz, $CDCl_3$) δ 27.20, 29.38, 30.95, 31.63, 32.21, 40.92, 50.75, 56.21, 74.94, 105.95, 115.66, 127.17, 136.18, 137.91, 139.62, 153.14, 162.35, 196.49. HRMS (m/z): calcd 1393.6543 (M+). Found: 1393.6500.
31. *Tetrapodal derivative: 9,9′,9″,9‴-(4,4′,4″,4‴-(benzene-1,2,4,5-tetrayltetrakis (methylene))tetrakis(oxy)tetrakis(benzene-4,1-diyl))tetrakis(3,3,6,6-tetramethyl-3,4,5,6,7,9-hexahydro-1H-xanthene-1,8(2H)-dione)* (**18**): White solid; mp 137–139 °C; ^{1}H NMR (400 Hz, $CDCl_3$) δ 0.99, 1.09 (s, 48H, CH_3), 2.19 (s, 16H, CH_2), 2.45 (s, 16H, CH_2), 4.69 (s, 4H, CH), 5.02 (s, 8H, CH_2), 6.79 (d, J = 6 Hz, 8H, ArH), 7.18 (d, J = 4.4 Hz, 8H, ArH), 7.58 (s, 2H, ArH); ^{13}C NMR (100 Hz, $CDCl_3$) δ 27.51, 29.22, 30.92, 32.23, 40.87, 50.79, 67.43, 114.42, 115.79, 129.36, 135.22, 136.89, 157.10, 162.13, 196.56. MALDI-TOF-MS (m/z): calcd 1631.9552 (M+K). Found: 1631.