Supplementary Information (SI) for Journal of Materials Chemistry A.

Supplementary Information: Data-Driven Design and Green Preparation of Bio-Based Flame Retardant Polyamide Composites

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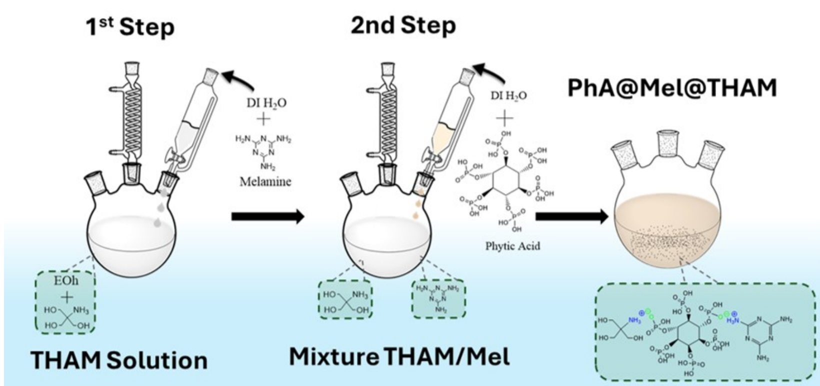

Figure 1: Reaction scheme of Pha@Mel@THAM

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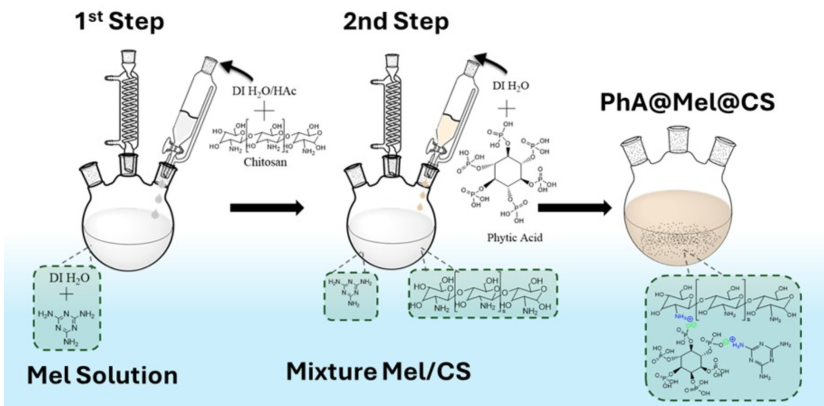


Figure 2: Reaction scheme of Pha@Mel@CS

Table. S1. Flame retardants synthesis summary

Flame retardant	Main components	FR Type	Reaction route	Ref
PhA-THAM	Phytic Acid Tris(hydroxymethyl) aminomethane	Organic phosphate and charring agent Fully Biobased	Ionic complexation Two-Step reaction	[1], 2020
HNT-PhA	Phytic Acid Halloysite nanoclay	Aluminosilicate clay and organic phosphate, Partially biobased	Ionic complexation Two-Step reaction	[2], 2023
HNT-CS	Chitosan Halloysite nanoclay	Aluminosilicate clay Aminobased polysaccharide Partially biobased	Ionic complexation Two-Step reaction	[3], 2012
HNT@PhA-CS	Phytic Acid Chitosan Halloysite nanoclay	Aluminosilicate clay, Organic phosphate, Aminobased polysaccharide, Partially biobased	Ionic complexation Three-Step reaction	[4], 2023
BN-PhA	Phytic Acid Boron Nitride	Organic phosphate Hexagonal boron and nitrogen layered sheets, Partially biobased	Assisted ball milling	[5], 2022
Mel-PhA	Phytic Acid Melamine	Organic phosphate, Blowing agent, Partially biobased	Ionic complexation Two-Step reaction	[6], 2018
HNT@Mel-PhA	Phytic Acid Melamine Halloysite nanoclay	Aluminosilicate clay, Organic phosphate, Blowing agent, Partially biobased	Ionic complexation Three-Step reaction	[7], 2019

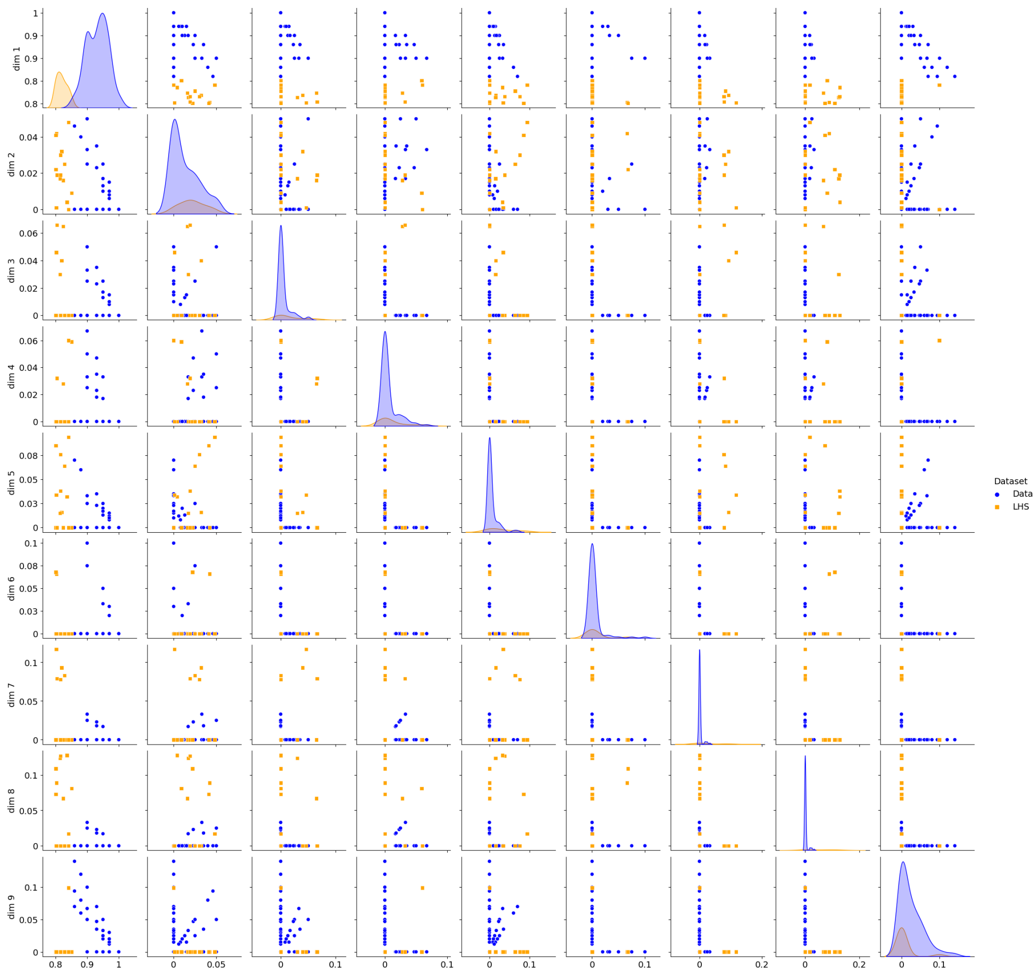


Figure 3: 15 $\text{CASTRO}_{\text{LHS}}$ suggestions in comparison to preliminary data. Dim 1,...,9 corresponds to PA-56, PhA, the amino-based components, i.e. CS, BN, THAM, and MEL, and the metal-containing components, i.e. CaBO, ZnBO, and HNT respectively.

Table. S2. Formulations of polyamide composites in first experimental run

Sample	PA56	PhA	Mel	THAM	CS	BN	ZNBO	CaBO	HNT	OP-935	OP-1400
1	100	-	-	-	-	-	-	-	-	-	-
2*	100	-	-	-	-	-	-	-	-	-	-
3	95	1.7	-	3.3	-	-	-	-	-	-	-
4	95	1.7	-	1.7	-	-	1.7	-	-	-	-
5	95	1.7	-	1.7	-	-	-	1.7	-	-	-
6	93	-	-	-	-	-	-	-	-	7.0	-
7	93	-	-	-	-	-	-	-	-	-	7.0
8	93	2.3	-	4.7	-	-	-	-	-	-	-
9	93	2.3	-	2.3	-	-	2.3	-	-	-	-
10	93	2.3	-	2.3	-	-	-	2.3	-	-	-
11	90	-	-	-	-	-	-	-	-	-	10
12	90	3.3	-	6.7	-	-	-	-	-	-	-
13	90	3.3	-	3.3	-	-	3.3	-	-	-	-
14	90	3.3	-	3.3	-	-	-	3.3	-	-	-
15	100	-	-	-	-	-	-	-	-	-	-
16	97	-	-	-	-	-	-	-	3	-	-
17	97	1	-	-	-	-	-	-	2	-	-
18	97	-	-	-	1.5	-	-	-	1.5	-	-
19	95	-	-	-	-	-	-	-	5	-	-
20	95	1.7	-	-	-	-	-	-	3.3	-	-
21	95	-	-	-	2.5	-	-	-	2.5	-	-
22	93	-	-	-	-	-	-	-	7	-	-
23	93	2.3	-	-	-	-	-	-	4.7	-	-
24	93	-	-	-	3.5	-	-	-	3.5	-	-
25	90	-	-	-	-	-	-	-	10	-	-
26	90	3.3	-	-	-	-	-	-	6.7	-	-
27	90	-	-	-	5.0	-	-	-	5.0	-	-
62	88	-	-	-	-	-	-	-	12	-	-
29	88	4	-	-	-	-	-	-	8	-	-
30	88	-	-	-	6	-	-	-	6	-	-
31	86	-	-	-	-	-	-	-	14	-	-
32	86	4.6	-	-	-	-	-	-	9.4	-	-
33	86	-	-	-	7	-	-	-	7	-	-
34	97	0.8	-	-	0.8	-	-	-	1.5	-	-
35	95	1.3	-	-	1.3	-	-	-	2.5	-	-

Table. S2. (CONT) Formulations of polyamide composites in first experimental run

Sample	PA56	PhA	Mel	THAM	CS	BN	ZNBO	CaBO	HNT	OP-935	OP-1400
36	90	2.5	-	-	2.5	-	-	-	5.0	-	-
37	97	0.8	0.8	-	-	-	-	-	1.5	-	-
38	95	1.3	1.3	-	-	-	-	-	2.5	-	-
39	90	2.5	2.5	-	-	-	-	-	5.0	-	-
40	97	-	-	-	-	3	-	-	-	-	-
41	97	1	-	-	-	2	-	-	-	-	-
42	95	-	-	-	-	5	-	-	-	-	-
43	95	1.7	-	-	-	3.3	-	-	-	-	-
44	90	-	-	-	-	10	-	-	-	-	-
45	90	2.5	-	-	-	7.5	-	-	-	-	-
46	93	3.5	-	3.5	-	-	-	-	-	-	-
47	93	3.5	-	1.8	-	-	1.8	-	-	-	-
48	93	3.5	-	1.8	-	-	-	1.8	-	-	-
49	90	5.0	-	5.0	-	-	-	-	-	-	-
50	90	5.0	-	2.5	-	-	2.5	-	-	-	-
51	90	5.0	-	2.5	-	-	-	2.5	-	-	-
52	97	1.5	1.5	-	-	-	-	-	-	-	-
53	95	2.5	2.5	-	-	-	-	-	-	-	-
54	90	5.0	5.0	-	-	-	-	-	-	-	-
55	97	0.6	-	-	1.2	-	-	-	1.2	-	-
56	95	1.0	-	-	2.0	-	-	-	2.0	-	-
57	90	2.5	-	-	2.5	-	-	-	5.0	-	-
58	95	-	-	-	-	-	-	-	-	5.0	-
59	95	-	-	-	-	-	-	-	-	-	5.0
60	97	-	-	-	1.0	-	-	-	2.0	-	-
61	95	-	-	-	1.7	-	-	-	3.3	-	-
62	93	-	-	-	2.3	-	-	-	4.7	-	-
63	90	-	-	-	3.3	-	-	-	6.7	-	-
64	97	1.5	-	-	-	-	-	-	1.5	-	-
65	95	2.5	-	-	-	-	-	-	2.5	-	-
66	93	3.5	-	-	-	-	-	-	3.5	-	-
67	90	5.0	-	-	-	-	-	-	5.0	-	-
68	97	-	1.5	-	-	-	-	-	1.5	-	-
69	95	-	2.5	-	-	-	-	-	2.5	-	-

Table. S2. (CONT) Formulations of polyamide composites in first experimental run

Sample	PA56	PhA	Mel	THAM	CS	BN	ZNBO	CaBO	HNT	OP-935	OP-1400
70	93	-	3.5	-	-	-	-	-	3.5	-	-
71	90	-	5.0	-	-	-	-	-	5.0	-	-
72	97	-	1.0	-	-	-	-	-	2.0	-	-
73	95	-	1.7	-	-	-	-	-	3.3	-	-
74	93	-	2.3	-	-	-	-	-	4.7	-	-
75	90	-	3.3	-	-	-	-	-	6.7	-	-

Table. S3. FTIR peaks assignment table

Peak position (cm^{-1})	Assingments	Spectra name	References
2690	P(=O)-OH	Phytic Acid	[8]
2315	P-O-H	Phytic Acid	[9]
1631	P-OH	Phytic Acid	[10]
954	P(=O)-OH	Phytic Acid	[9]
898	Stretching of C—O	THAM	[11]
1748	Deformation vibration of N—H	THAM	[11]
2938	Stretching OH group	THAM	[11]
3346	Stretching primary amine group	THAM	[1]
772	Deformation of trizaine ring	Melamine	[7]
1436	Vibration of triazine ring	Melamine	[7]
3317	Stretching N-H group	Melamine	[7]
3465	Stretching N-H group	Melamine	[7]
1316	Stretching vibration of amide I group	Chitosan	[12]
1637	C-N stretching of amide III group	Chitosan	[13]
2891	Stretching vibration of CH group	Chitosan	[13]
2897	Stretching vibration of CH2 group	Chitosan	[13]

Table. S4. Formulations of polyamide composites by RF modeling (Batch 1)

Sample	PA56	PhA	Mel	THAM	CS	BN	ZNBO	CaBO	HNT
91	94.1	0.4	-	-	0.4	-	-	-	5.1
92	96.5	0.7	-	0.5	0.7	-	-	-	1.6
93	96.8	0.7	-	0.2	0.8	-	-	-	1.5
94	96.9	0.7	0.2	-	0.6	-	-	-	1.6
95	96.5	0.7	0.4	-	0.8	-	-	-	1.6
96	97	0.7	0.1	-	0.7	-	-	-	1.5

Table. S5. Formulations of polyamide composites by RF modeling (Batch 2)

Sample	PA56	PhA	Mel	THAM	CS	BN	ZNBO	CaBO	HNT
97	96.8	0.8	-	0.3	0.7	-	-	-	1.4
98	96.7	0.8	-	0.3	0.8	-	-	-	1.4
99	96.7	0.8	-	0.1	1	-	-	-	1.4
100	96.4	0.8	0.4	-	1	-	-	-	1.4
101	96.8	0.8	-	-	1	-	-	-	1.4
102	96.7	0.8	0.1	-	1	-	-	-	1.4

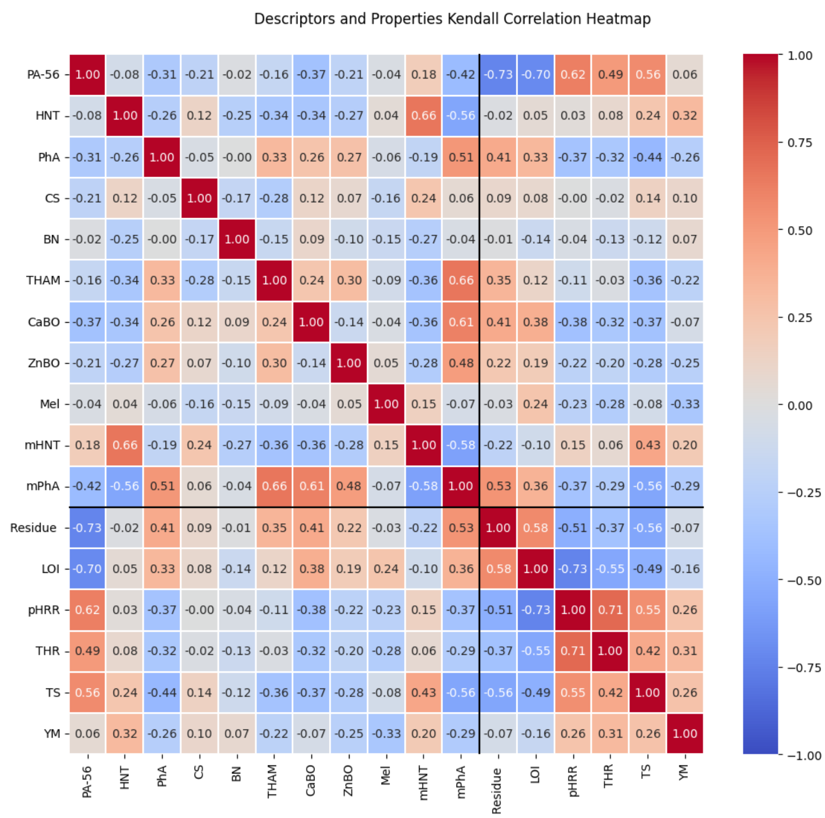


Figure 4: Kendall correlation between the descriptors (PA-56, HNT, PhA, CS, BN, THAM, CaBO, ZnBO, Mel, mHNT, mPhA) and properties (Residue, LOI, pHRR, THR, TS, YM). PA-56 is the main factor for fire properties, while HNT is relevant for YM. Fire properties are cross-correlated but TS and YM are only slightly correlated.

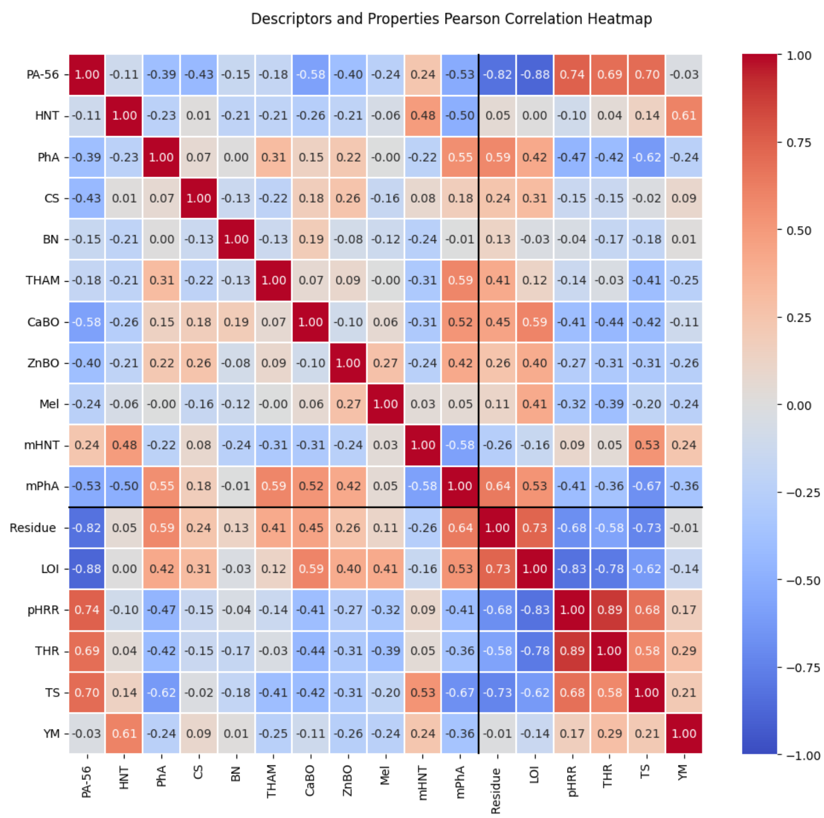
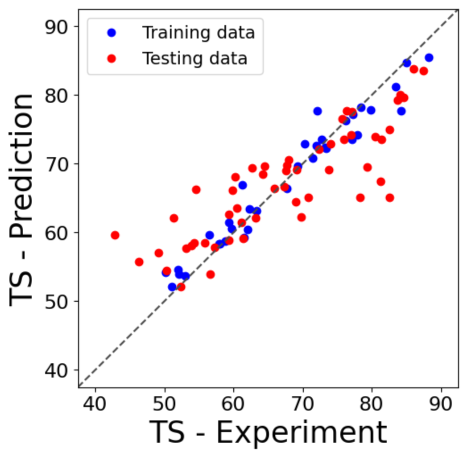
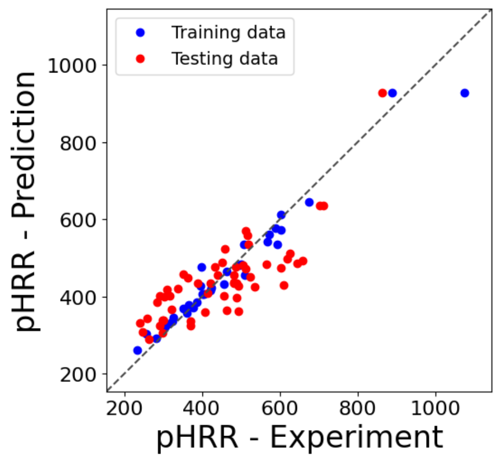


Figure 5: Pearson correlation between the descriptors (PA-56, HNT, PhA, CS, BN, THAM, CaBO, ZnBO, Mel, mHNT, mPhA) and properties (Residue, LOI, pHRR, THR, TS, YM). PA-56 is most influential for fire properties, while HNT is key for YM. Fire properties are highly interrelated, and mechanical properties are also cross-correlated.

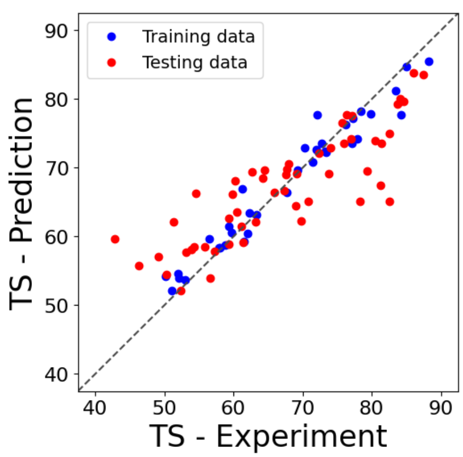


(a) TS single-task.

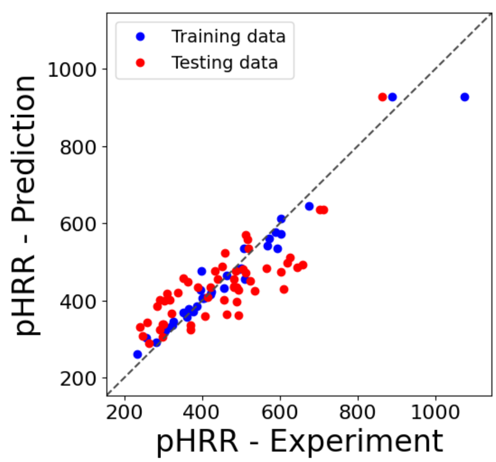


(b) pHRR single-task

Figure 6: Comparison of prediction and experimental data for single-task.



(a) TS multi-task.



(b) pHRR multi-task

Figure 7: Comparison of prediction and experimental data for multi-task.

References

[1] Y. X. Yang, L. Haurie, J. Zhang, X. Q. Zhang, R. Wang and D. Y. Wang, *Express Polymer Letters*, 2020, **14**, 705–716.

[2] J. Feng, W. Luo, W. He, X. Ai and P. Song, *Polymer Degradation and Stability*, 2023, **217**, 110509.

[3] R. Zhai, B. Zhang, Y. Wan, C. Li, J. Wang and J. Liu, *Chemical Engineering Journal*, 2013, **214**, 304–309.

[4] Q. Zhao, X. Cheng, J. Kang, L. Kong, X. Zhao, X. He and J. Li, *International Journal of Biological Macromolecules*, 2023, **246**, 125682.

[5] Q. Bao, R. He, Y. Liu and Q. Wang, *Composites Part A: Applied Science and Manufacturing*, 2023, **164**, 107309.

[6] L. Adlnasab, M. Ezoddin, R. A. Shojaei and F. Aryanasab, *Journal of Chromatography B*, 2018, **1095**, 226–234.

[7] S. Shang, X. Ma, B. Yuan, G. Chen, Y. Sun, C. Huang, S. He, H. Dai and X. Chen, *Composites Part B: Engineering*, 2019, **177**, 107371.

[8] F. Qi, Z. Xia, J. Jin, X. Fu, W. Wei, S. Wang and G. Sun, *ACS Applied Materials and Interfaces*, 2018, **10**, 2819–2827.

[9] G. Yin, J. Hobson, Y. Duan and D.-Y. Wang, *SSRN Electronic Journal*, 2021.

[10] G. Yin, D. Zhao, X. Wang, Y. Ren, L. Zhang, X. Wu, S. Nie and Q. Li, *RSC Advances*, 2015, **5**, 79070–79080.

[11] R. Wu and Y. Yao, 2013 International Conference on Materials for Renewable Energy and Environment, 2013, pp. 613–616.

[12] M. Fernandes Queiroz, K. Melo, D. Sabry, G. Sassaki and H. Rocha, *Marine Drugs*, 2014, **13**, 141–158.

[13] T. Zhang, H. Yan, L. Shen, Z. Fang, X. Zhang, J. Wang and B. Zhang, *Industrial and Engineering Chemistry Research*, 2014, **53**, 19199–19207.