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Gram-scale synthesis of porphycenes through acid-catalyzed oxidative macrocyclizations of *E*/*Z*-mixed 5,6-diaryldipyrroethenes†

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The gram-scale production of porphycene derivatives is reported. This has been achieved by acid-catalyzed ring closure of an *E*/*Z*-mixture of 5,6-diaryldipyrroethenes, resulting in the formation of *meso*-tetraarylporphycenes in yields of up to 80%. *E*/*Z*-isomerization of the 5,6-diaryldipyrroethenes under acidic conditions was key to proceed the effective macrocyclization.

Porphycene, the first structural isomer of porphyrin, was reported in 1986 (ref. 1) and has since been the subject of extensive study.[2] Porphycene derivatives have attracted considerable attention in photodynamic therapy,[3] protein mimicry,[4–7] catalysis,[8,9] tautomerism,[10–12] and materials chemistry.[13,14] Various porphycenes with *meso*- and β-substituents and their metal complexes have been reported to have tunable functionalities, crystallinities and solubilities.[15–31]

However, the main obstacle to the widespread application of porphycenes is the lack of efficient and economical methods for their production. Therefore, porphycene chemistry has advanced more slowly than that of the parent isomer porphyrin. The gram-scale synthesis of porphycenes has yet to be reported, despite reports of gram-scale synthesis of other tetrapyrrole macrocycles, such as porphyrin,[32,33] corrole,[34] and norcorrole.[35] The first reported synthetic approach (Fig. 1, Method a) proposed by Vogel in 1986, is recognized as the standard preparation method.[1] This method is based on the McMurry reductive cyclization of two 5,5′-diacyl-2,2′-bipyrroles. However, this synthesis is very difficult owing to the susceptibility of pyrrole intermediates to rapid oxidation in air and the unimpressive yields obtained. The final McMurry cyclization is difficult to scale up and usually gives very low yields. An alternative approach (Fig. 1, Method b) was proposed by Srinivasan in 2008.[36] This synthesis of 9,10,19,20-tetraarylporphycenes involves the formation of two 2,2′-linkages followed by aromatization. It also includes an oxidative ring closure reaction of 5,6-diaryldipyrroethanes with *p*-toluenesulfonic acid (*p*-TSA) as acid catalyst, followed by oxidation with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ). In 2014, Ravikanth optimized the same methodology using 5,6-diaryldipyrroethenes as precursors with a wider scope of aryl substituents.[37] However, these alternative systems have not been explored further, probably due to the last oxidative macrocyclization step giving a low yield of 3–7%.[36,37]

Inspired by these reports, we have recently demonstrated the syntheses of 9,10,19,20-tetralkylporphycenes through the oxidative macrocyclization of 5,6-dialkyldipyrroethenes as precursors.[38] The coupling reaction of 5,6-dialkyldipyrroloethenes with *p*-TSA as acid catalyst, followed by oxidation with DDQ, was unsuccessful. In contrast, the coupling reaction of 5,6-dialkyldipyrroloethene with hypervalent iodine(III) reagent, [bis(trifluoroacetoxyiodo)]benzene (PIFA), as oxidant, followed by autooxidation in air, was successful, affording 9,10,19,20-tetralkylporphycenes in 3–13% yields.[38] These findings indicated that careful selection of the macrocyclization/oxidation conditions was important in the alternative strategy (Fig. 1, Method b). From this background, we now report a highly efficient and gram-scale production of porphycene derivatives based on this alternative strategy. Notably, yields of the oxidative macrocyclization of 5,6-diaryldipyrroethenes were dramatically increased to up to 80%, and

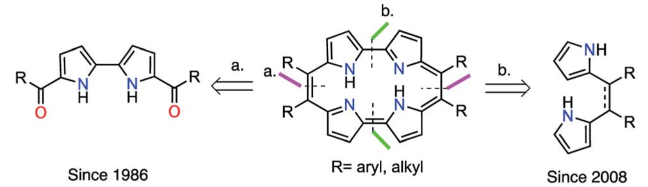

Fig. 1 Retrosynthetic analysis of porphycenes.

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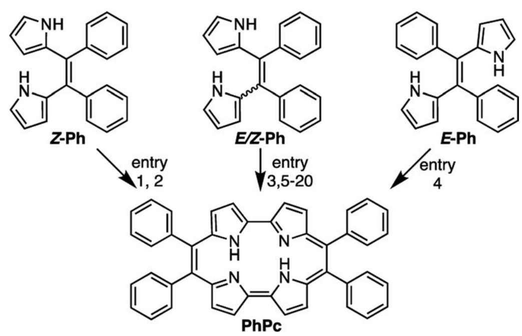
the gram-scale production of novel porphycenes was demonstrated. To our knowledge, such a high-yielding scalable synthesis of porphycenes has not previously been reported.[2]

The *E*/*Z* mixture of 5,6-diphenyldipyrroloethene (**Ph**) was synthesized from commercially available 2-benzoylpyrrole (**1**) using a McMurry coupling in the presence of Zn and $TiCl_4$ in THF. The *E*/*Z* isomer ratio of the mixture was determined to be 2 : 1 by integrating the pyrrole α-H proton signals in the ^{1}H NMR spectra. We successfully separated the *E*- and *Z*-isomers from the mixture by a silica gel column chromatography. The (*E*)-5,6-diaryldipyrroethanes (***E*-Ph**) and (*Z*)-5,6-diaryldipyrroethanes (***Z*-Ph**) were characterized according to the previous reports.[39]

First, we investigated optimizing the oxidative macrocyclizations using the synthesis of 9,10,19,20-tetrphenylporphycenes (**PhPc**) as the model reaction (Table 1). According to the previous reports, the coupling reaction of ***Z*-Ph** with *p*-TSA as acid catalyst, followed by oxidation with DDQ was performed to give **PhPc** in 5% yield (Table 1, entry 1). This result was consistent with previous results.[37] In contrast, the coupling reactions of ***Z*-Ph** with *p*-TSA followed by oxidation with *p*-chloranil produced **PhPc** in 45% yield (entry 2). The coupling reaction of ***E*/*Z*-Ph** with *p*-TSA followed by oxidation with *p*-chroranil produced **PhPc** in 35% yield (entry 3), while that of ***E*-Ph** with *p*-TSA followed by oxidation with *p*-chloranil produced the target porphycene in 30% yield (entry 4). In porphycene synthesis, coupling two ***E*-Ph** molecules is expected not to result in macrocycles, but linear polymers such as polypyrroles. However, as shown in entries 3 and 4, the efficient synthesis of porphycenes proceeded from ***E*-Ph**. The ^{1}H NMR spectra of CD_2Cl_2 solutions of ***E*-Ph**, ***Z*-Ph**, and ***E*/*Z*-Ph** showed negligible *E*/*Z*-isomerization at room temperature in the dark after 1 day (Fig. S1–S3†). Therefore, we surmised that the isomers interconverted in the presence of *p*-TSA in CH_2Cl_2. Indeed, it has been reported that compounds containing alkene in its structure undergoes *E*/*Z*-isomerization by proton *in situ*.[40] *E*/*Z*-isomerization of **Ph** under acidic condition was also supported by density-functional theory calculations (Fig. S34 and Table S5, see detail in ESI†). A plausible mechanism for formation of porphycenes are shown in Fig. 2. The acid (proton) plays two important roles: *E*/*Z* isomerization and oxidative ring closure reaction of 5,6-diaryldipyrroloethene.

To further enhance the yield of **PhPc**, the oxidants, solvents, and acid catalysts were optimized. First, the trial experiments with ***E*/*Z*-Ph** were conducted with *p*-TSA as acid catalyst in CH_2Cl_2 followed by treatment with different oxidants (Table 1, entry 3 and 5–8). Oxidants *p*-chloranil, quinone, bromanil, fluoranil, and *o*-chloranil gave **PhPc** yields of 35%, 14%, 42%, 32%, and 17%, respectively, when using *p*-TSA (0.5 eq.) as catalyst. The results indicated oxidation required a moderate oxidant, with too strong or too weak oxidants decreasing the **PhPc** yield. However, when toluene was used as solvent, **PhPc** was afforded with a significantly decreased yield of 6% (entry 10). Furthermore, when the amount of *p*-TSA was increased from 0.5 eq. to 1.0 eq., 2.0 eq., and 10 eq., the yields of **PhPc** clearly fluctuated from 35% to 50%, 65%, and 8%, respectively (entries 11–13). Furthermore, using a stronger Brønsted acid, trifluoromethane sulfonic acid (TfOH; 0.5 eq.), as catalyst gave the **PhPc** in

Table 1 Screening of reaction conditions for the synthesis of PhPc[a]



Entry	Pyrrole	Acid[b]	Oxidant	Solvent	Yield[c] (%)
1	***Z*-Ph**	*p*-TSA	DDQ	CH_2Cl_2	5
2	***Z*-Ph**	*p*-TSA	*p*-Chloranil	CH_2Cl_2	45
3	***E*/*Z*-Ph**	*p*-TSA	*p*-Chloranil	CH_2Cl_2	35
4	***E*-Ph**	*p*-TSA	*p*-Chloranil	CH_2Cl_2	30
5	***E*/*Z*-Ph**	*p*-TSA	Quinone	CH_2Cl_2	14
6	***E*/*Z*-Ph**	*p*-TSA	Bromanil	CH_2Cl_2	42
7	***E*/*Z*-Ph**	*p*-TSA	Fluoranil	CH_2Cl_2	32
8	***E*/*Z*-Ph**	*p*-TSA	*o*-Chloranil	CH_2Cl_2	17
9	***E*/*Z*-Ph**	*p*-TSA	*p*-Chloranil	$CHCl_3$	32
10	***E*/*Z*-Ph**	*p*-TSA	*p*-Chloranil	Toluene	6
11	***E*/*Z*-Ph**	*p*-TSA[d]	*p*-Chloranil	CH_2Cl_2	50
12	***E*/*Z*-Ph**	*p*-TSA[e]	*p*-Chloranil	CH_2Cl_2	65
13	***E*/*Z*-Ph**	*p*-TSA[f]	*p*-Chloranil	CH_2Cl_2	8
14	***E*/*Z*-Ph**	TfOH	*p*-Chloranil	CH_2Cl_2	62
15	***E*/*Z*-Ph**	TfOH[e]	*p*-Chloranil	CH_2Cl_2	6
16	***E*/*Z*-Ph**	TFA	*p*-Chloranil	CH_2Cl_2	6
17	***E*/*Z*-Ph**	TFA[e]	*p*-Chloranil	CH_2Cl_2	18
18	***E*/*Z*-Ph**	$BF_3 \cdot Et_2O$	*p*-Chloranil	CH_2Cl_2	30
19	***E*/*Z*-Ph**	$BF_3 \cdot Et_2O$[e]	*p*-Chloranil	CH_2Cl_2	8

[a] Reaction conditions: [pyrrole] = 1.6×10^{-3} M; [acid] = 0.5 eq. to pyrrole; [Oxidant] = 3 eq. to pyrrole; room temperature. [b] Abbreviations: *p*-TSA, *p*-toluenesulfonic acid monohydrate; TfOH trifluoromethane sulfonic acid; TFA, trifluoroacetic acid. [c] Yield of isolated product. [d] [Acid] = 1.0 eq. to pyrrole. [e] [Acid] = 2.0 eq. to pyrrole. [f] [Acid] = 10 eq. to pyrrole.

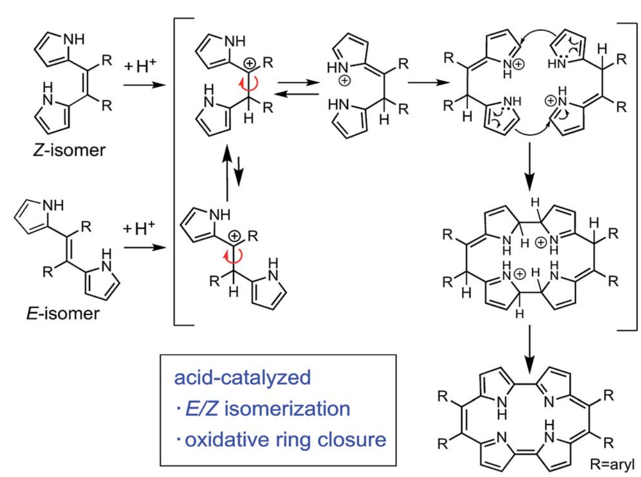


Fig. 2 Plausible mechanism for the formation of porphycenes.

a reasonably good yield of 62% (entry 14). However, the yield decreased to 6% when 2.0 eq. of TfOH was used (entry 15). A weaker Brønsted acid, trifluoroacetic acid (TFA), was also tested, affording **PhPc** in lower yields of 6% (0.5 eq.) or 18% (2.0 eq.) (entries 16 and 17). Lewis acid catalyst $BF_3 \cdot Et_2O$ (0.5 eq.) gave **PhPc** in a moderate yield of 30% (entry 18). The yield was decreased to 8% when the amount of $BF_3 \cdot Et_2O$ was increased to 2.0 eq. (entry 19). The coupling reaction was also performed using PIFA as oxidant, which produced **PhPc** in 1% yield (see ESI†). Based on these results, we selected *p*-TSA as acid catalyst, *p*-chloranil as oxidant, and CH_2Cl_2 as solvent as the optimal reaction conditions.

Next, we attempted to broaden the reaction scope to the synthesis of *meso*-tetraarylporphycenes with various aryl-substituents. Considering the solubility and electronic control of the porphycene framework, we attempted to synthesize a set of new *meso*-tetraaryl substituted porphycenes bearing 3,5-bis(trifluoromethy)phenyl (**CF$_3$Pc**) and 3,5-difluorophenyl groups (**FPc**) as electron-withdrawing groups, and 3,5-dimethyphenyl groups (**CH$_3$Pc**) as electron-donating groups (Fig. 3(a)). The starting materials (**1–4**) were obtained in 54–68% yields. Compounds **1–4** were then subjected to the McMurry coupling conditions. A conventional workup gave *E*/*Z* mixtures of the corresponding dipyrroethenes (***E*/*Z*-Ph**, ***E*/*Z*-CF$_3$**, ***E*/*Z*-F**, and ***E*/*Z*-CH$_3$**) in yields of 42–67%. Finally, optimizations of oxidative macrocyclizations afforded porphycenes (**PhPc**, **CF$_3$Pc**, **FPc**, and **CH$_3$Pc**) in yields of 46–80%. Notably, the yields of **CF$_3$Pc** and **FPc** were 80% and 72%, respectively. Therefore, we had succeeded in preparing **PhPc**, **CF$_3$Pc**, and **FPc** with isolated yields of 0.90 g, 1.06 g, and 1.42 g. The overall yield of **FPc** from pyrrole and 3,5-difluorobenzoyl chloride was 27%. This is an unprecedented result that enables the gram-scale synthesis of porphycene derivatives in high yields. These compounds were characterized by ^1H, ^{13}C, and ^{19}F NMR spectroscopy and high-resolution mass analysis (Fig. S4–S30†).

Single crystals of porphycenes were fully characterized (Fig. 3(b) and Tables S1–S4†).‡ The molecular structures exhibited perfect rectangular cores in **PhPc** (N1⋯N2 2.874(5) Å; N1⋯N3 2.547(6) Å), **CF$_3$Pc** (N1⋯N2 2.894(8) Å; N1⋯N3 2.552(8) Å), **FPc** (N1⋯N2 2.866(3) Å; N1⋯N3 2.562(4) Å), and **CH$_3$Pc** (N1⋯N2 2.873(2) Å; N1⋯N3 2.568(2) Å). Side views of the porphycene derivatives showed that **PhPc** and **FPc** had planar geometries, while **CF$_3$Pc** and **CH$_3$Pc** showed slightly distorted structures due to steric repulsion between the bulky 3,5-di(trifluoromethyl) or 3,5-dimethylphenyl substituents in the crystals.

The optoelectronic properties of the porphycenes were also investigated (Table 2). The porphycenes generally showed a strong Soret band at approximately 380 nm and three weak Q bands in the region of 578–654 nm (Fig. S31†). The introduction of electron-withdrawing groups (**CF$_3$Pc**, **FPc**) resulted in a hypochromic shift in the absorption spectra, while introducing electron-rich groups (**CH$_3$Pc**) resulted in a bathochromic shift. The compounds were reasonably fluorescent, with a strong fluorescence band at approximately 660 nm and a shoulder band at approximately 720 nm. The quantum yields of porphycenes in CH_2Cl_2 were in the range 16.0–29.2%, and the lifetimes were in the range of 2.4–5.6 ns (Fig. S32†). The electrochemical properties of the porphycenes were characterized by cyclic voltammetry and differential pulse voltammetry in CH_2Cl_2 *vs.* Ag/AgCl (Fig. S33†). All porphycenes displayed the typical two reversible one-electron reductions and one reversible and/or quasi-reversible one-electron oxidation. Owing to the presence of electron-withdrawing groups for **CF$_3$Pc** and **FPc**, the first oxidation and first reduction potentials were more positive and less negative, respectively, compared with those of **PhPc**. Conversely, owing to the presence of electron-rich groups for **CH$_3$Pc**, the first oxidation and first reduction potentials were

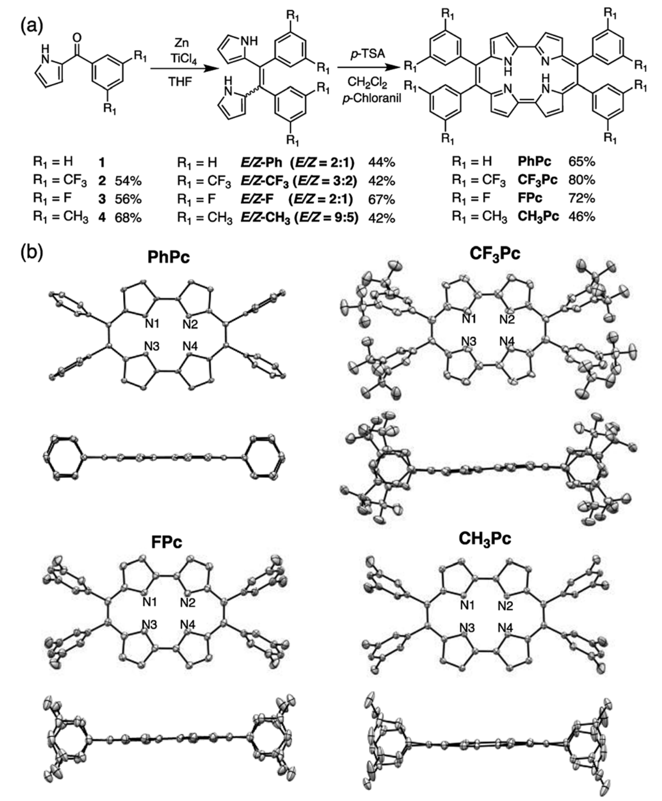


Fig. 3 (a) Synthesis of *meso*-tetraarylporphycenes, (b) single-crystal X-ray structures of PhPc, CF$_3$Pc, FPc, and CH$_3$Pc (above) top view and (below) side view. Thermal ellipsoids are drawn at the 50% probability level. For clarity, only N atoms are numbered and hydrogen atoms are omitted.

‡ Crystal data for **PhPc** (from $CHCl_3$/methanol): $C_{44}H_{30}N_4 \cdot 2(CHCl_3)$, $M_w = 853.46$, triclinic, space group $P\bar{1}$, $a = 9.235(16)$, $b = 9.638(17)$, $c = 11.86(2)$ Å, $\alpha = 78.93$, $\beta = 76.86(5)$, $\gamma = 73.21(4)^\circ$, $V = 975(3)$ Å^3, $Z = 1$, $T = 100$ K, $D_c = 1.158$ g cm^{-3}, GOF = 1.107, $R_1 = 0.0618$ and w$R_2 = 0.1604$ for all data, CCDC 1868296. Crystal data for **CF$_3$Pc** (from CH_2Cl_2/methanol): $C_{52}H_{22}F_{24}N_4$, $M_w = 1158.74$, monoclinic, $C2/c$, $a = 35.48(3)$, $b = 14.931(11)$, $c = 8.852(6)$ Å, $\beta = 99.42(2)^\circ$, $V = 4626(6)$ Å^3, $Z = 4$, $T = 103$ K, $D_c = 1.664$ g cm^{-3}, GOF = 1.031, $R_1 = 0.0988$ and w$R_2 = 0.2659$ for all data, CCDC 1868292. Crystal data for **FPc** (from $C_2H_4Cl_2$/methanol): $C_{24}H_{22}F_8N_4 \cdot 0.793(C_2H_4Cl_2)$, $M_w = 837.12$, monoclinic, $P21/c$, $a = 8.4081(6)$, $b = 13.0237(9)$, $c = 17.9996(12)$ Å, $\beta = 103.022(2)^\circ$, $V = 1920.4(2)$ Å^3, $Z = 2$, $T = 103$ K, $D_c = 1.448$ g cm^{-3}, GOF = 1.073, $R_1 = 0.0566$ and w$R_2 = 0.1716$ for all data, CCDC 1868294. Crystal data for **CH$_3$Pc** (from THF/methanol): $C_{52}H_{46}N_4$, $M_w = 726.93$, monoclinic, $P21/n$, $a = 8.7406(11)$, $b = 15.369(2)$, $c = 16.406(2)$ Å, $\beta = 103.303(4)^\circ$, $V = 2144.8(5)$ Å^3, $Z = 2$, $T = 103$ K, $D_c = 1.126$ g cm^{-3}, GOF = 1.095, $R_1 = 0.0611$ and w$R_2 = 0.1848$ for all data, CCDC 1868293.

Table 2 Summary optoelectronic properties of porphycenes

	Soret band[a] [nm]	Q bands[a] [nm]	λ_{em} [nm]	Φ_{PL}[b] [%]	τ[c] [ns]	Reduction $E_{1/2}$/V *vs.* Ag/AgCl		Oxidation $E_{1/2}$/V *vs.* Ag/AgCl	HOMO–LUMO gap
						E_{red} [V] I	E_{red} [V] II	E_{ox} [V]	ΔE_{red-ox} [V]
PhPc	381 (5.1)	584 (4.2), 625 (4.4), 653 (4.6)	667, 727	16.0	2.6	−0.73	−0.98	+1.14	1.87
CH_3Pc	384 (5.1)	578 (4.3), 619 (4.4), 648 (4.6)	655, 721	29.2	5.6	−0.51	−0.81	+1.59	2.10
FPc	381 (5.1)	578 (4.3), 619 (4.4), 647 (4.5)	655, 720	17.5	3.4	−0.59	−0.88	+1.33	1.92
CH_3Pc	383 (5.1)	586 (4.3), 627 (4.5), 654 (4.6)	655, 727	15.2	2.4	−0.76	−1.08	+1.06	1.82

[a] Values parentheses correspond to log. [b] Absolute photoluminescence quantum yields. [c] Fluorescence lifetime.

less negative and more positive over **PhPc**. The HOMO–LUMO energy gaps of porphycene derivatives ($\Delta E = E_{ox1} - E_{red1}$) were 2.10, 1.92, 1.87, and 1.82 V for **CF_3Pc**, **FPc**, **PhPc**, and **CH_3Pc**, respectively. The optoelectronic properties were supported by DFT calculations (Tables S6–S8, Fig. S35†).

In conclusion, *meso*-tetraarylporphycenes were synthesized on a gram-scale in a few steps with high overall yields using an optimized acid-catalyzed oxidative macrocyclization of *E*/*Z*-mixtures of 5,6-diaryldipyrroethene. *E*/*Z*-isomerization of the 5,6-diaryldipyrroethenes under acidic conditions was key to effective macrocyclization, as supported by both experimental and theoretical observations. The straightforward production of porphycenes will enable practical applications of porphycene derivatives.

Conflicts of interest

There were no conflicts to declare.

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Notes and references

1 E. Vogel, M. Köcher, H. Schmickler and J. Lex, *Angew. Chem., Int. Ed.*, 1986, **25**, 257–259.
2 G. Anguera and D. Sanchez-Garcia, *Chem. Rev.*, 2017, **117**, 2481–2516.
3 J. C. Stockert, M. Canete, A. Juarranz, A. Villanueva, R. W. Horobin, J. Borrell, J. Teixido and S. Nonell, *Curr. Med. Chem.*, 2007, **14**, 997–1026.
4 T. Hayashi, H. Dejima, T. Matsuo, H. Sato, D. Murata and Y. Hisaeda, *J. Am. Chem. Soc.*, 2002, **124**, 11226–11227.
5 K. Oohora, Y. Kihira, E. Mizohata, T. Inoue and T. Hayashi, *J. Am. Chem. Soc.*, 2013, **135**, 17282–17285.
6 K. Oohora, H. Meichin, Y. Kihira, H. Sugimoto, Y. Shiro and T. Hayashi, *J. Am. Chem. Soc.*, 2017, **139**, 18460–18463.
7 K. Oohora, H. Meichin, L. Zhao, M. W. Wolf, A. Nakayama, J. Y. Hasegawa, N. Lehnert and T. Hayashi, *J. Am. Chem. Soc.*, 2017, **139**, 17265–17268.
8 W.-C. Lo, C.-M. Che, K.-F. Cheng and T. C. Mak, *Chem. Commun.*, 1997, 1205–1206.
9 T. Koide, I. Aritome, T. Saeki, Y. Morita, Y. Shiota, K. Yoshizawa, H. Shimakoshi and Y. Hisaeda, *ACS Omega*, 2018, **3**, 4027–4034.
10 J. Waluk, *Chem. Rev.*, 2017, **117**, 2447–2480.
11 T. Kumagai, F. Hanke, S. Gawinkowski, J. Sharp, K. Kotsis, J. Waluk, M. Persson and L. Grill, *Nat. Chem.*, 2013, **6**, 41–46.
12 J. N. Ladenthin, T. Frederiksen, M. Persson, J. C. Sharp, S. Gawinkowski, J. Waluk and T. Kumagai, *Nat. Chem.*, 2016, **8**, 935–940.
13 W. Brenner, J. Malig, R. D. Costa, D. M. Guldi and N. Jux, *Adv. Mater.*, 2013, **25**, 2314–2318.
14 R. D. Costa, J. Malig, W. Brenner, N. Jux and D. M. Guldi, *Adv. Mater.*, 2013, **25**, 2600–2605.
15 E. Vogel, M. Balci, K. Pramod, P. Koch, J. Lex and O. Ermer, *Angew. Chem., Int. Ed.*, 1987, **26**, 928–931.
16 E. Vogel, M. Köcher, J. Lex and O. Ermer, *Isr. J. Chem.*, 1989, **29**, 257–266.
17 E. Vogel, P. Koch, X. L. Hou, J. Lex, M. Lausmann, M. Kisters, M. A. Aukauloo, P. Richard and R. Guilard, *Angew. Chem., Int. Ed.*, 1993, **32**, 1600–1604.
18 D. Kuzuhara, J. Mack, H. Yamada, T. Okujima, N. Ono and N. Kobayashi, *Chem.–Eur. J.*, 2009, **15**, 10060–10069.
19 T. Sarma, P. K. Panda, P. T. Anusha and S. V. Rao, *Org. Lett.*, 2011, **13**, 188–191.
20 A. Rana and P. K. Panda, *Org. Lett.*, 2014, **16**, 78–81.
21 A. Rana, S. Lee, D. Kim and P. K. Panda, *Chem. Commun.*, 2015, **51**, 7705–7708.
22 A. Rana and P. K. Panda, *Chem. Commun.*, 2015, **51**, 12239–12242.
23 M. Duran-Frigola, R. Tejedor-Estrada, D. Sanchez-Garcia and S. Nonell, *Phys. Chem. Chem. Phys.*, 2011, **13**, 10326–10332.
24 K. Oohora, A. Ogawa, T. Fukuda, A. Onoda, J. Y. Hasegawa and T. Hayashi, *Angew. Chem., Int. Ed.*, 2015, **54**, 6227–6230.
25 O. Planas, D. Fernandez-Llaneza, I. Nieves, R. Ruiz-Gonzalez, E. Lemp, A. L. Zanocco and S. Nonell, *Phys. Chem. Chem. Phys.*, 2017, **19**, 25537–25543.

26 D. Kuzuhara, M. Sakaguchi, W. Furukawa, T. Okabe, N. Aratani and H. Yamada, *Molecules*, 2017, **22**, 908.
27 T. Ono, D. Koga, K. Yoza and Y. Hisaeda, *Chem. Commun.*, 2017, **53**, 12258–12261.
28 V. Roznyatovskiy, V. Lynch and J. L. Sessler, *Org. Lett.*, 2010, **12**, 4424–4427.
29 L. Cuesta, E. Karnas, V. M. Lynch, P. Chen, J. Shen, K. M. Kadish, K. Ohkubo, S. Fukuzumi and J. L. Sessler, *J. Am. Chem. Soc.*, 2009, **131**, 13538–13547.
30 M. Abe, H. Futagawa, T. Ono, T. Yamada, N. Kimizuka and Y. Hisaeda, *Inorg. Chem.*, 2015, **54**, 11061–11063.
31 T. Sarma, B. S. Kumar and P. K. Panda, *Angew. Chem., Int. Ed.*, 2015, **54**, 14835–14839.
32 A. D. Adler, F. R. Longo, J. D. Finarelli, J. Goldmach, J. Assour and L. Korsakoff, *J. Org. Chem.*, 1967, **32**, 476.
33 J. S. Lindsey, H. C. Hsu and I. C. Schreiman, *Tetrahedron Lett.*, 1986, **27**, 4969–4970.
34 B. Koszarna and D. T. Gryko, *J. Org. Chem.*, 2006, **71**, 3707–3717.
35 T. Ito, Y. Hayashi, S. Shimizu, J. Y. Shin, N. Kobayashi and H. Shinokubo, *Angew. Chem., Int. Ed.*, 2012, **51**, 8542–8545.
36 K. Anju, S. Ramakrishnan, A. P. Thomas, E. Suresh and A. Srinivasan, *Org. Lett.*, 2008, **10**, 5545–5548.
37 E. Ganapathi, T. Chatterjee and M. Ravikanth, *Eur. J. Org. Chem.*, 2014, **2014**, 6701–6706.
38 T. Ono, D. Koga and Y. Hisaeda, *Chem. Lett.*, 2017, **46**, 260–262.
39 K. Garg, E. Ganapathi, P. Rajakannu and M. Ravikanth, *Phys. Chem. Chem. Phys.*, 2015, **17**, 19465–19473.
40 A. Souizi, A. Robert, P. Batail and L. Ouahab, *J. Org. Chem.*, 1987, **52**, 1610–1611.