

ASIAN JOURNAL OF CHEMISTRY



https://doi.org/10.14233/ajchem.2021.23056

Microwave Assisted Synthesis of Dibenzo-[b,f][1,5]diazocine Derivatives for Photocatalytic Water Splitting Applications

S.K. Cho¹, J.H. Jung², Y. Sissembayeva³, J.H. Song², D.I. Jung² and Y.H. Hwang^{3,*}

Received: 9 November 2020;

Accepted: 16 January 2021;

Published online: 16 February 2021;

AJC-20260

Photocatalytic water splitting converts solar energy to storable hydrogen molecules which has the highest energy per mass. Most catalysts for photocatalytic water splitting utilize noble metals or precious metals. Organic photocatalysts are attracting more attention owing to several advantages like light weight, low cost, defined structure and tunability. In this study, the synthesis of several dibenzo[b_f][1,5]-diazocines via microwave irradiation for water splitting application is reported. Microwave irradiation facilitates fast, safe and simple synthesis in green reaction conditions. Mini library of dibenzo[b_f][1,5]diazocines were created in order to understand substituents effect on the photocatalytic activity.

Keywords: Dibenzo[b,f][1,5]diazocines, Microwave irradiation, Green synthesis, Self-condensation, Water splitting.

INTRODUCTION

The production of hydrogen gas by catalytic water splitting under solar light irradiation gives a sustainable way to clean energy technologies [1,2]. The development of an efficient, stable, economic, and eco-friendly catalyst is of vital importance. Inorganic catalysts such as platinum-based catalysts are considered to be the most effective catalysts, however, high cost and scarcity have called for possible alternatives [3,4]. As a result, numerous efforts are put into developing metal-free organic catalysts for the hydrogen evolution reaction.

Although most studies are focused on highly conjugated polymers such as linear poly(phenylene)s, promising works on small molecule organic photocatalysts having narrow π - π * energy gaps are being reported benefitting from low cost and easy processability [5-7]. Organic synthesis in general require large amount of solvents which is somewhat paradoxical considering the fact that the bigger picture is to develop catalysts for ecofriendly energy production. Therefore, we used microwave irradiation which do not require any solvent. Conventional reactions are often carried out in solution using large quantities

of toxic reagents and require high temperature and long reaction time.

However, under microwave irradiation, reaction proceed to completion within minutes without harsh conditions (high heat and toxic solvents). Moreover, this kind of reaction reduces side reactions and hence increases yields [8]. In this paper, the synthesis of dibenzo[b,f][1,5]diazocines via microwave irradiation is reported. Microwave irradiation allowed fast and efficient synthesis without the need for any organic solvent or high reaction temperature in appreciable yield. To increase the π -conjugation length, styrene and 4-vinylbiphenyl were first conjugated to 2-aminobenzophenones. Direct conjugation to diazocine ring approach was also compared as well as the effect on the self-condensation when different positions on the diazocine ring are modified. UV-visible absorption was studied to check the potential for the water splitting applications.

EXPERIMENTAL

All chemicals including 2-amino-4'-bromobenzophenone, 2-amino-5-bromobenzophenone and diphenyl phosphate

This is an open access journal, and articles are distributed under the terms of the Attribution 4.0 International (CC BY 4.0) License. This license lets others distribute, remix, tweak, and build upon your work, even commercially, as long as they credit the author for the original creation. You must give appropriate credit, provide a link to the license, and indicate if changes were made.

¹Crystal Bank Research Institute, Pusan National University, Miryang, 50463, Republic of Korea

²Department of Chemistry, Dong-A University, Busan, 49315, Republic of Korea

³Department of Nano Energy Engineering, Pusan National University, Busan 46241, Republic of Korea

^{*}Corresponding author: Fax: +82 51 5142358; Tel: +82 51 5103184, E-mail: yhwang@pusan.ac.kr

628 Cho et al. Asian J. Chem.

(DPP) were obtained from Sigma-Aldrich (St Louis, USA) and used as received without further purification.

¹H & ¹³C NMR spectra were obtained with Agilent MR400 DD2 (400 MHz) spectrometers. UV absorption spectra were recorded using JASCO V-770 UV-Vis spectrophotometer.

Synthesis of (*E*)-(2-aminophenyl)(4-styrylphenyl)-methanone (1): 2-Amino-4'-bromobenzophenone (3 mmol), styrene (3 mmol), K_2CO_3 (6 mmol) and palladium(II) acetate (0.05 mmol) were dissolved in 10 mL of DMF and reacted at 100 °C for 12 h under nitrogen atmosphere. Resulting reaction mixture was filtered and purified by column chromatography (ethyl acetate/*n*-hexane = 1/9, v/v) to afford (*E*)-(2-aminophenyl)-(4-styrylphenyl)methanone (1). Yield: 79%; pale yellow solid; ¹H NMR (DMSO, 400 MHz): δ 7.74 (d, J = 8.3 Hz, 2H), 7.63 (d, J = 8.5 Hz, 2H) 7.58 (d, J = 8.2 Hz, 2H), 7.41(m, 4H), 7.32 (m, 3H), 7.04 (s, 2H), 6.86 (d, J = 7.6Hz, 1H), 6.54(t, J = 6.9 Hz, 1H); ¹³C NMR (DMSO, 400 MHz): δ 197.7, 152.2, 140.4, 139.2, 137.3, 134.7, 131.0, 129.9, 129.3, 128.6, 128.1, 127.3, 126.7, 117.4, 117.1, 114.7.

Synthesis of (*E*)-(4-(2-([1,1'-biphenyl]-4-yl)vinyl)-phenyl)(2-aminophenyl)methanone (2): 2-Amino-4'-bromobenzophenone (3 mmol), 4-vinylbiphenyl (6 mmol), K_2CO_3 (6 mmol) and palladium(II) acetate (0.05 mmol) were dissolved in 10 mL of DMF and reacted at 100 °C for 12 h under nitrogen. Resulting reaction mixture was filtered and purified by column chromatography (ethyl acetate/*n*-hexane = 1/9, v/v) to afford (*E*)-(4-(2-([1,1'-biphenyl]-4-yl)vinyl)phenyl)(2-aminophenyl)methanone (2). Yield: 32.5%; pale yellow solid; ¹H NMR (DMSO, 400 MHz): δ 7.73 (m, 8H), 7.57 (d, *J* = 8.3Hz, 2H) 7.48 (m, 2H), 7.44 (m, 2H), 7.37 (m, 1H), 7.30 (m, 2H), 7.04 (s, NH₂), 6.86 (m, 1H), 6.52 (m, 1H); ¹³C NMR (DMSO, 400 MHz): δ 197.6, 152.1, 140.2, 140.0, 139.9, 139.0, 136.3, 134.5, 134.0, 130.4, 129.8, 129.4, 128.0, 127.8, 127.4, 126.9, 126.6, 119.9, 116.9, 114.6.

Synthesis of (*E*)-(2-amino-5-styrylphenyl)(phenyl)-methanone (3): 2-Amino-5-bromobenzophenone (3 mmol), styrene (3 mmol), K_2CO_3 (6 mmol) and palladium(II) acetate (0.05 mmol) were dissolved in 10 mL of DMF and reacted at 100 °C for 12 h under nitrogen. Resulting reaction mixture was filtered and purified by column chromatography (ethyl acetate/n-hexane = 1/9, v/v) to afford (*E*)-(2-aminophenyl)(5-styrylphenyl)methanone (3). Yield: 72.3 %; pale yellow solid; ${}^{1}H$ NMR (DMSO, 400 MHz): δ 7.71(d, J = 8.7 Hz, 1H), 7.59 (m, 3H), 7.54 (m, 2H), 7.47 (d, J = 7.4 Hz, 2H), 7.40 (d, J = 19 Hz, 1H), 7.29 (m, 4H), 7.17(t, J = 7.3 Hz, 1H), 7.02 (d, J = 16.4 Hz, 1H), 6.89(m, 2H); ${}^{13}C$ NMR (DMSO, 400 MHz): δ 198.1, 152.0, 140.2, 137.9, 133.5, 131.6, 131.5, 129.2, 128.9, 128.7, 127.2, 126.4, 124.6, 123.8, 118.1, 116.5.

Synthesis of (E)-(5-(2-([1,1'-biphenyl]-4-yl)vinyl)-2-aminophenyl)(phenyl)methanone (4): 2-Amino-5-bromobenzophenone (3 mmol), 4- vinylbiphenyl (6 mmol), K_2CO_3 (6 mmol) and palladium(II) acetate (0.05 mmol) were dissolved in 10 mL of DMF and reacted at 100 °C for 12 h under nitrogen. Resulting reaction mixture was filtered and purified by column chromatography (ethyl acetate/n-hexane = 1/9, v/v) to afford (E)-(5-(2-([1,1'-biphenyl]-4-yl)vinyl)-2-aminophenyl)(phenyl)methanone (4). Yield : 28.5 %; pale yellow solid; ¹H NMR

(DMSO, 400 MHz): δ 7.72 (m, 1H), 7.36 (m, 2H), 7.60 (m, 6H), 7.55(m, 2H), 7.45 (m, 3H), 7.34 (m, 3H), 7.13 (d, J = 16.3 Hz, NH₂), 6.95 (d, J = 3.7 Hz, 1H), 6.91(d, J = 3.8 Hz, 1H); 13 C NMR (DMSO, 400 MHz): δ 198.1, 152.1, 140.2, 140.1, 138.7, 137.2, 133.5, 131.63, 131.6, 129.4, 129.2, 128.8, 127.7, 127.2, 126.9, 126.7, 124.1, 123.9, 118.1, 116.5.

Synthesis of (5Z,11Z)-6,12-bis(4-((E)-styryl)phenyl)**dibenzo**[b,f][1,5]diazocine (5): (E)-(2-Aminophenyl)(4-styrylphenyl)methanone (1) (3 mmol) was self-condensed in the presence of catalyst diphenylphosphate (DPP) (35 mmol) via microwave irradiation (RE-555 TCW, Samsung) for 1 min. Resulting reaction mixture was diluted with 100 mL of ethyl acetate, neutralized with 25 mL of 10 % NaOH and extracted with ethyl acetate three times, washed with water and dried using MgSO₄. Product was purified by column chromatography (ethyl acetate/n-hexane = 1/9, v/v) to give (5Z,11Z)-6,12-bis(4-((E)-styryl)phenyl)dibenzo[b,f][1,5]diazocine (5). Yield: 63.4 %; pale yellow solid; ¹H NMR (DMSO, 400 MHz): δ 7.65 (s, 8H), 7.59 (m, 4H), 7.36 (m, 7H), 7.28 (m, 6H), 7.08 (m, 2H), 7.03 $(d, J = 1.5 \text{ Hz}, 2H), 7.01 (d, J = 1.8 \text{ Hz}, 1H); {}^{13}\text{C NMR (DMSO},$ 400 MHz): $\delta 168.6$, 151.9, 140.6, 137.1, 136.5, 130.9, 130.3, 129.7, 129.2, 128.5, 127.9, 127.8, 127.2, 126.9, 126.5, 124.8, 121.0.

Synthesis of (5Z,11Z)-6,12-bis(4-((E)-styryl)phenyl)**dibenzo**[*b*,*f*][1,5]diazocine (6): (*E*)-(4-(2-([1,1'-Biphenyl]-4yl)vinyl)phenyl)(2-aminophenyl)methanone (2) (1 mmol) was self-condensed in the presence of catalyst DPP (15 mmol) via microwave irradiation (RE-555 TCW, Samsung) for 1 min. Resulting reaction mixture was diluted with 100 mL of ethyl acetate, neutralized with 25 mL of 10 % NaOH and extracted with ethyl acetate three times, washed with water and dried using MgSO₄. Product was purified by column chromatography (ethyl acetate/n-hexane = 1/9, v/v) to give (5Z,11Z)-6,12-bis(4-((E)-styryl)phenyl)dibenzo[b,f][1,5]diazocine (6). Yield: 60.8 %; pale yellow solid; ¹H NMR (DMSO, 400 MHz): δ 7.80 (m, 5H), 7.51 (m, 3H), 7.41 (m, 14H), 7.31 (t, J = 7.3 Hz, 6H), 7.21 (m, 2H), 7.11 (d, J = 1.5 Hz, 2H), 7.07 (s,1H), 7.05 (s, 1H), 6.96(s, 4H); ¹³C NMR (DMSO, 400 MHz): δ 160.5, 154.5, 133.0, 131.0, 129.6, 128.8, 128.5, 128.44, 128.4, 127.7, 126.5, 125.9. 121.7.

Synthesis of (5Z,11Z)-6,12-diphenyl-2,8-di((E)-styryl)**dibenzo**[b,f][1,5]**diazocine** (7): (E)-(2-Aminophenyl)(5-styrylphenyl)methanone (3) (3 mmol) was self-condensed in the presence of catalyst DPP (35 mmol) via microwave irradiation (RE-555 TCW, Samsung) for 1 min. Resulting reaction mixture was diluted with 100 mL of ethyl acetate, neutralized with 25 mL of 10% NaOH and extracted with ethyl acetate three times, washed with water and dried using MgSO₄. Product was purified by column chromatography (ethyl acetate/n-hexane = 1/9, v/v) to give (5Z,11Z)-6,12-diphenyl-2,8-di((E)-styryl)dibenzo-[b,f][1,5]diazocine (7). Yield: 58.6 %; pale yellow solid; ¹H NMR (DMSO, 400 MHz): δ 7.69 (m, 4H), 7.67 (d, J = 1.8 Hz, 1H), 7.64 (d, J = 1.8 Hz, 1H), 7.52 (m, 6H), 7.45 (m, 4H), 7.32(m, 4H), 7.26 (d, J = 1.8 Hz, 2H), 7.21 (m, 2H), 7.17 (d, J = 1.8 Hz, 2H)1.0 Hz, 4H), 7.08 (s, 1H), 7.06 (s, 1H); ¹³C NMR (DMSO, 400 MHz): δ 151.0, 137.5, 137.4, 133.3, 132.0, 129.3, 129.1, 128.7, 128.3, 128.0, 127.6, 127.1, 126.8, 125.7, 121.6.

Synthesis of (5Z,11Z)-2,8-bis((E)-2-([1,1'-biphenyl]-4-yl)vinyl)-6,12-diphenyldibenzo[b,f][1,5]diazocine (8): (E)-

(4-(2-([1,1'-Biphenyl]-4-yl)vinyl)phenyl)(2-aminophenyl)methanone (**4**) (1 mmol) was self-condensed in the presence of catalyst DPP (15 mmol) *via* microwave irradiation (RE-555 TCW, Samsung) for 1 min. Resulting reaction mixture was diluted with 100 mL of ethyl acetate, neutralized with 25 mL of 10 % NaOH and extracted with ethyl acetate three times, washed with water and dried using MgSO₄. Product was purified by column chromatography (ethyl acetate/*n*-hexane = 1/9, v/v) to give (5*Z*,11*Z*)-2,8-*bis*((*E*)-2-([1,1'-biphenyl]-4-yl)vinyl)-6,12-diphenyldibenzo[*b*,*f*][1,5]diazocine (**8**). Yield: 59.8 %; pale yellow solid; ¹H NMR (DMSO, 400 MHz): δ 7.67 (m, 20H), 7.45 (m, 5H), 7.36 (m, 7H), 7.10 (t, J = 7.4 Hz, 2H), 7.05 (m, 4H); ¹³C NMR (DMSO, 400 MHz): δ 151.9, 140.6, 140.0, 139.9, 136.5, 136.2, 130.4, 129.7, 129.4, 128.0, 127.8, 127.3, 127.0, 126.9, 126.5, 124.0, 121.9, 121.1, 121.0.

RESULTS AND DISCUSSION

Our group have previously published Friedlander condensation of 2-aminobenzophenones with various heteroaromatic

ketones via microwave irradiation to obtain quinoline derivatives [9,10]. Dibenzo[b,f][1,5]diazocines were obtained as minor products with relatively low yields. When 2-aminobenzophenone was self-condensed in the presence of acid catalyst, DPP [11] via microwave irradiation, dibenzo[b,f][1,5]diazocine was obtained in high yield (89.4%) (Fig. 1) [12]. Conventional dibenzo[b,f][1,5]diazocine synthesis methods required long reflux times [13], whereas microwave assisted reaction method dramatically changed to solventless, no-heat-required and 1 min reaction.

2-Aminobenzophenone derivatives, 2-amino-4'-bromobenzophenone and 2-amino-5-bromobenzophenone were first reacted with styrene or 4-phenylstyrene to give products **1-4** (Fig. 2). We tried self-condensation of 2-amino-4'-bromobenzophenone and 2-amino-5-bromobenzophenone first and subsequent modification to extend the degree of conjugation. Our hypothesis was that this method would avoid unfavored steric hindrance during the dibenzo[*b*,*f*][1,5]diazocine cyclization because it was found that steric hindrance significantly

Fig. 1. Self-condensation mechanism of 2-aminobenzophenones (1-4) to yield dibenzo[b,f][1,5]diazocines (5-8)

Fig. 2. Synthetic route to dibenzo[b,f][1,5]diazocine compound (6)

630 Cho et al. Asian J. Chem.

lowered or even prevented self-condensation in previous studies [9]. Interestingly, this strategy was not successful probably due to three molecules having to collide together in order to form the desired products. Therefore, 2-aminobenzophenone derivatives were modified first (products 1-4) to elongate the π - π conjugation prior to dibenzo[b,f][1,5]diazocine synthesis (Fig. 2).

Modified 2-aminobenzophenone derivatives **1-4** were further self-condensed to afford dibenzo[b,f][1,5]diazocines **5-6** (Fig. 2). Contrary to our expectation, prior modification did not stop the subsequent reaction. Dibenzo[b,f][1,5]diazocines **5-6** were synthesized in acceptable yields (\sim 60%) compared to the unmodified dibenzo[b,f][1,5]diazocine (89.4%) as shown in Table-1. In general, 4'-modified benzophenones **1** and **2** gave better yields to products **5** and **6** (63.4 and 60.8%, respectively) than 5-modified benzophenones **3** and **4** to products **7** and **8** (58.6 and 59.7%, respectively). This can be explained by the structure of products. Products **7** and **8** have 4 substituents on the non-planar dibenzo[b,f][1,5]diazocine ring whereas products **5** and **6** have only 2 substituents (Fig. 3). Four bulky substituents on such non-planar ring causes steric hindrance and therefore is probably less favored [14,15].

TABLE-1							
SELF-CONDENSATION OF 2-AMINOBENZOPHENONES							
(1-4) UNDER MW IRRADIATION TO							
DIBENZO[b , f][1,5]DIAZOCINE PRODUCTS 5-8							
Product	Catalyst	2-Aminobenzoph	- Yield (%				
		v	37	Ticiu (/			

	Product	Catalyst -	2-Ammobenzophenones			Yield (%)a
				X	Y	Tielu (%)
	5	DPP	1	Styryl	Н	63.4
	6	DPP	2	Biphenyl	Н	60.8
	7	DPP	3	Н	Styryl	58.6
	8	DPP	4	Н	Biphenyl	59.7
^a Isolated yields						

Lastly, dibenzo [b,f] [1,5] diazocines with different conjugation lengths were subjected to UV-visible spectroscopy to study the potential on the photocatalytic activity (Fig. 4). UVvis absorption shifted to the visible range as the conjugation length increased (from 300 nm to 400 nm and 430 nm). This result is similar to other small molecular weight organic molecules applied for the water splitting use [7]. The UV-Vis absorption results show promising potential for photocatalytic activity. Moreover, presence of nitrogen is reported to enhance interactions with inorganic nanoparticles such as Pt which can result in improved catalytic activity and durability when made into a composite [16,17]. As a matter of fact, prepared dibenzo [b,f]-[1,5]diazocines (5-8) exhibited excellent stability toward acidic (pH 3), basic (pH 10) and even in electrolyte (NaCl) environments under both sunlight and UV irradiation (data not shown). Photocatalysts generally show high efficiency in acidic or basic conditions [18]. However, these conditions compromise the stability of most catalysts especially in combination with the electrolytes. Therefore, the excellent stability of dibenzo[b,f][1,5]diazocines show promising potential for hydrogen generation. Subsequent study of dibenzo [b,f][1,5] diazocines applied into water splitting device are underway.

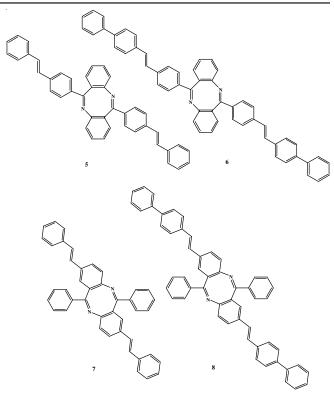


Fig. 3. Structure of four different dibenzo[b,f][1,5]diazocines (5-8)

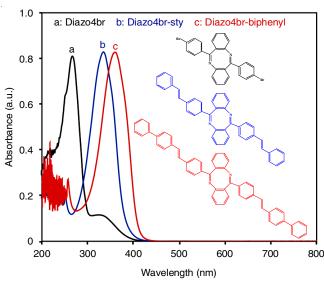


Fig. 4. UV-vis absorption spectra of dibenzo [b,f][1,5] diazocine compounds as conjugation length increases

Conclusion

In conclusion, dibenzo[b,f][1,5]diazocine derivatives with extended degree of conjugation were prepared via microwave irradiation. Microwave assisted reaction allowed fast and simple synthesis without the need of organic solvent or high temperature. It was found that pre-modification and subsequent self-condensation was a better way to prepare dibenzo[b,f][1,5]diazocines than post-modification. Moreover, having less number of substituents on the dibenzo[b,f][1,5]diazocine ring was favoured in yields. UV-Vis absorption spectra and excellent stability in acidic, basic and electrolyte environment showed

the promising potential of resulting products for the water splitting applications.

ACKNOWLEDGEMENTS

This work was supported by a 2-Year Research Grant of Pusan National University.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

REFERENCES

- M.G. Walter, E.L. Warren, J.R. McKone, S.W. Boettcher, Q. Mi, E.A. Santori and N.S. Lewis, *Chem. Rev.*, 110, 6446 (2010); https://doi.org/10.1021/cr1002326
- A. Kudo and Y. Miseki, *Chem. Soc. Rev.*, 38, 253 (2009); https://doi.org/10.1039/B800489G
- C. Jiang, S.J.A. Moniz, A. Wang, T. Zhang and J. Tang, *Chem. Soc. Rev.*, 46, 4645 (2017); https://doi.org/10.1039/C6CS00306K
- H.W. Seo and J.S. Kim, *Appl. Sci. Converg. Technol.*, 27, 61 (2018); https://doi.org/10.5757/ASCT.2018.27.4.61
- G. Zhang, Z.A. Lan and X. Wang, *Angew. Chem. Int. Ed.*, 55, 15712 (2016); https://doi.org/10.1002/anie.201607375
- L. Yao, A. Rahmanudin, N. Guijarro and K. Sivula, *Adv. Energy Mater.*, 8, 1802585 (2018); https://doi.org/10.1002/aenm.201802585

- A. Aleksovska, P. Lonnecke, M.A. Addicoat, R. Glaser and E. Hey-Hawkins, *ChemistryOpen*, 9, 405 (2020); https://doi.org/10.1002/open.202000036
- W. Cieslik, M. Serda, A. Kurczyk and R. Musiol, *Curr. Org. Chem.*, 17, 491 (2013);
 - https://doi.org/10.2174/1385272811317050006
- S.K. Cho, J.H. Song, E.J. Lee, D.H. Lee, J.T. Hahn and D.I. Jung, *Bull. Korean Chem. Soc.*, 36, 2746 (2015); https://doi.org/10.1002/bkcs.10557
- D.I. Jung, J.H. Song, E.J. Lee, Y.Y. Kim, D.H. Lee, Y.G. Lee and J.T. Hahn, *Tetrahedron Lett.*, 50, 5805 (2009); https://doi.org/10.1016/j.tetlet.2009.07.150
- G. Sabitha, R.S. Babu, B.V. Subba Reddy and J.S. Yadav, *Synth. Commun.*, 29, 4403 (1999); https://doi.org/10.1080/00397919908086603
- L. Perreux and A. Loupy, *Tetrahedron*, 57, 9199 (2001); https://doi.org/10.1016/S0040-4020(01)00905-X
- X. Wang, J. Li, N. Zhao and X. Wan, Org. Lett., 13, 709 (2011); https://doi.org/10.1021/o1102957c
- Y. Jiang, X. Wang, Z. An and X. Wan, Tetrahedron Lett., 55, 3545 (2014); https://doi.org/10.1016/j.tetlet.2014.04.094
- Y.N. Liu, J.Z. Li and X.B. Wan, Chin. J. Polym. Sci., 36, 736 (2018); https://doi.org/10.1007/s10118-018-2062-6
- Y. Chen, J. Wang, H. Liu, R. Li, X. Sun, S. Ye and S. Knights, *Electrochem. Commun.*, 11, 2071 (2009); https://doi.org/10.1016/j.elecom.2009.09.008
- F. Su, Z. Tian, C.K. Poh, Z. Wang, S.H. Lim, Z. Liu and J. Lin, *Chem. Mater.*, 22, 832 (2010); https://doi.org/10.1021/cm901542w
- S. Esiner, R.E.M. Willems, A. Furlan, W. Li, M.M. Wienk and R.A.J. Janssen, J. Mater. Chem. A Mater. Energy Sustain., 3, 23936 (2015); https://doi.org/10.1039/C5TA07325A