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Exploration of the reaction of potassium organotrifluoroborates with porphyrins

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ABSTRACT

A general method that uses potassium organotrifluoroborates in the Suzuki–Miyaura cross-coupling reaction with ring-brominated porphyrins has been investigated. The reaction conditions tolerate various functional groups and are applicable to the meso- and β-position as well as to aryl- and alkyl-substituted porphyrins. Depending on the nature of the potassium organotrifluoroborate, the coupling products can be obtained in yields of up to 75%.

The development of new synthetic pathways and strategies in the field of porphyrin chemistry is important for continued growth of their applications in industries and medicine. Depending on the substitution pattern, different porphyrins are widely used in various areas ranging from photophysics (nonlinear optics), electron transfer (solar energy conversion), to medicinal chemistry (photodynamic therapy).[1]

Amphiphilic porphyrins are of special interest in the field of photodynamic therapy.[2] The design of these compounds requires the introduction of alkyl substituents onto the porphyrin moiety as a crucial step. However, apart from total synthesis, only a limited number of procedures are available to generate alkyl-substituted porphyrins. One of the most common methods is the use of alkyllithium reagents which is limited to certain functional groups.[3] Hence, there is a need for the development of alternative pathways towards alkyl-substituted porphyrins.

One of the most straightforward methods for the design of new compounds is the use of C–C coupling reactions. Among palladium-catalyzed reactions, the Suzuki cross-coupling reaction is very popular in porphyrin chemistry.[4] Interestingly, arylboronic derivatives are used predominantly in these reactions as coupling partners with halogenated porphyrins. So far, there is only one example that has been reported previously where a porphyrin was reacted with an alkylboronic acid, namely the reaction of methylboronic acid with a β-brominated porphyrin.[5] This lack of examples is probably due to the fact that cross-coupling reactions using alkyl-metallic compounds have proven problematic as the organopalladium intermediates can undergo β-hydride elimination.[6] However, it has been shown in other areas that the use of potassium organotrifluoroborates instead of boronic acids or esters offers various advantages.[6] The most significant benefit is their higher air stability. Additionally, there are a number of commercially available potassium organotrifluoroborates that cannot be obtained as the boronic acid or ester analogue due to their instability.

In relation to our ongoing development of new metal-mediated reactions on porphyrins,[7,8] we have undertaken a study of the reaction of potassium organotrifluoroborates with porphyrins. Only one example using zinc-metallated porphyrins has been reported previously,[9] however, this involved the reaction with a brominated meso-phenyl ring targeted at cationic porphyrins. Here, we present a detailed study of the reaction of various potassium organotrifluoroborates, focusing on the use of potassium alkyltrifluoroborates with free-base porphyrins directly brominated in the meso- and β-position and containing aryl and alkyl substituents as well as different substitution patterns.

For ease of comparison with literature data, the reaction of 5-bromo-10,15,20-tris(4-methyphenyl)porphyrin[8] **1** (see Fig. 1) with potassium vinyltrifluoroborate was chosen as a model reaction.

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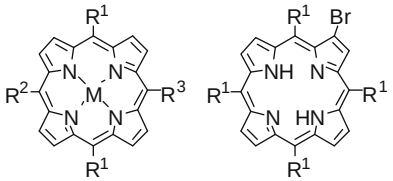
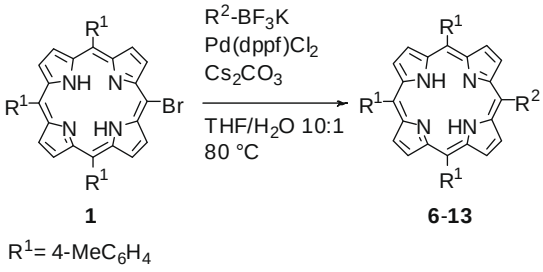


1-**4** **5**

1 $R^1 = R^2 = 4\text{-MeC}_6H_4$; R^3 = Br; M = 2H
2 $R^1 = 4\text{-MeC}_6H_4$; $R^2 = R^3$ = Br; M = 2H
3 $R^1 = R^2 = n\text{-}C_6H_{13}$; R^3 = Br; M = 2H
4 $R^1 = R^2 = 4\text{-MeC}_6H_4$; R^3 = I; M = Ni(II)
5 R^1 = Ph

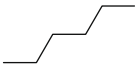
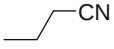
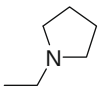
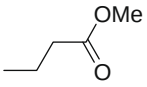
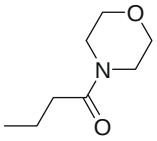
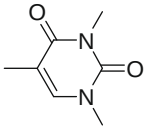
Figure 1. Structures of the starting materials.

After optimizing the reaction conditions of Molander et al.[10,11] for the Suzuki couplings involving meso-porphyrins,[12] 5,10,15-tris(4-methylphenyl)-20-vinylporphyrin **6** was obtained in 61% yield (Scheme 1).[13] The reaction of potassium vinyltrifluoroborate at the meso-bromophenyl position of [5-(4-bromophenyl)-10,15,20-tri(4-pyridyl)porphyrinato]zinc(II) gave the vinylphenyl analogue in 56% yield.[9] The synthesis of 5,10,15-tris(4-methylphenyl)-20-vinylporphyrin **6** using the boronic ester analogue, namely vinylboronic acid pinacol ester, was reported earlier by us in 52% yield.[8] This result is in agreement with observations made by Molander and co-workers that potassium trifluoroborates give slightly higher yields than their boronic acid or ester analogues.[10]



1 **6**-**13**

R^1= 4-MeC_6H_4

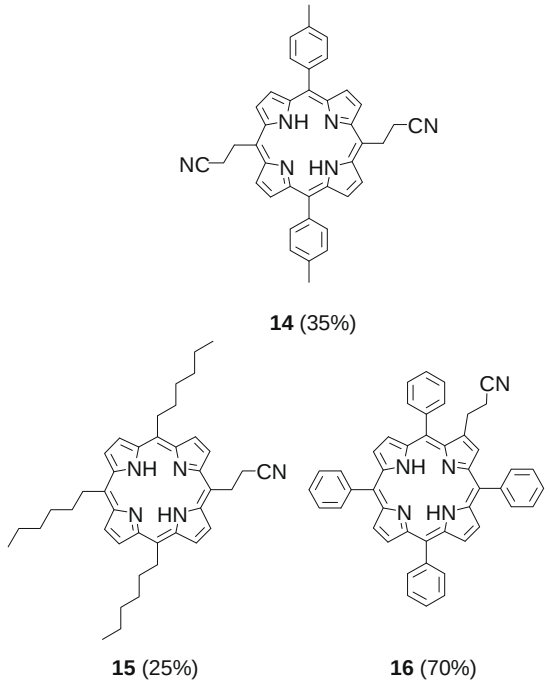
R^2	Product	Yield [%]
	**6**	61
	**7**	21
Me	**8**	29
	**9**	73
	**10**	26
	**11**	16[a]
	**12**	21
	**13**	75

Scheme 1. Reaction of potassium organotrifluoroborates with 5-bromo-10,15,20-tris(4-methylphenyl)porphyrin. Reaction conditions: bromoporphyrin (1 equiv), potassium organoborate (10 equiv, [a]20 equiv), Cs_2CO_3 (20 equiv), $Pd(dppf)Cl_2$ (25 mol %).

Encouraged by this result, various potassium organotrifluoroborates were subjected to the same reaction conditions (Scheme 1). All the reactions were carried out in a sealed Schlenk tube and reaction mixtures were heated until completion (monitored by TLC). Apart from compound **7**, with a reaction time of two days, all the reactions were complete within 12 h. The reaction conditions were tolerant towards various functional groups with yields ranging from moderate to good.[14] Note, that the potassium organotrifluoroborates used for the synthesis of compounds **9**–**13** are not commercially available as their boronic acid or ester analogues and thus the present approach offers significant advantages. Usually, the synthesis of compounds **7**–**13** would include several steps. An alternative pathway for the synthesis of **8** could be provided by the use of MeLi in S_NAr reactions. However, this presents problems through multiple reactions at the meso-position.[15]

To investigate the general applicability of the reaction conditions for porphyrins with other substitution patterns, 5,15-dibromo-10,20-bis(4-methylphenyl)porphyrin **2**,[7a] 5-bromo-10,15,20-trihexylporphyrin **3**[8] and 2-bromo-5,10,15,20-tetraphenylporphyrin **5**[16] were reacted with potassium cyanoethyltrifluoroborate to give compounds **14**–**16**, respectively (Fig. 2).[17] In the case of the dibrominated starting material, the amounts of potassium cyanoethyltrifluoroborate and cesium carbonate were doubled according to the number of bromide substituents. Compounds **14** and **15** were obtained in lower yields than **16**. Surprisingly, the difference in the reaction at the meso-position versus the β-position is very small and compound **16** was obtained in a yield comparable to that for **9**.

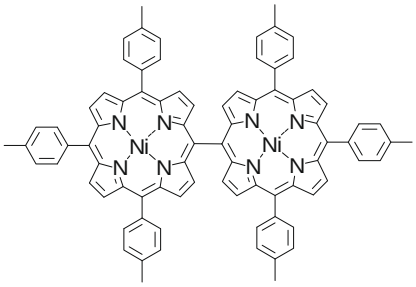
In an attempt to synthesize a methyl-bridged porphyrin dimer, compound **1** was reacted with potassium bromomethyltrifluoroborate. However, as no reaction was observed and only starting



14 (35%)

15 (25%) **16** (70%)

Figure 2. Cyano derivatives.



17 (10 %)

Figure 3. Bisporphyrin **17**.

material was recovered, a more reactive porphyrin, namely [5-iodo-10,15,20-tris(4-methylphenyl)porphyrinato]nickel(II) **4**, was subjected to the same reaction conditions. Surprisingly, the only product obtained was the directly meso–meso-linked bisporphyrin **17** in 10% yield (Fig. 3). The reaction mechanism remains unclear but investigations are going on. Possibly, a radical dimerization took place similar to that reported previously in oxidative coupling reactions.[7b,18]

In conclusion, we have presented a detailed investigation of the reaction of various potassium organotrifluoroborates with directly brominated porphyrins. The method is generally applicable to the meso- and β-position of the macrocycle as well as to aryl- and alkyl-substituted porphyrins with different substitution patterns. The reaction conditions tolerate various functional groups and depending on the nature of the potassium organotrifluoroborate, the new compounds were obtained in moderate to good yields. As potassium organotrifluoroborates offer a good alternative to boronic acids or esters, many of which are commercially available, we believe this method presents a useful tool for the synthesis of novel porphyrins and we are currently expanding the scope of this application.

Acknowledgement

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13. *General procedure*: A 20 mL Schlenk tube was flushed with argon and charged with porphyrin (30 mg, 1 equiv) and Cs_2CO_3 (20 equiv) in THF/H_2O (10:1, v/v). The solution was degassed via three freeze-pump-thaw cycles and was placed under argon. Potassium organotrifluoroborate (10 equiv) and Pd(dppf)Cl_2 (0.25 equiv) were added and the reaction mixture was heated to 80 °C overnight. The solvent was removed and the residue was dissolved in dichloromethane. The crude product was washed with a saturated solution of sodium bicarbonate, water and brine. The organic phase was dried over magnesium sulfate, the solvent was evaporated and the crude product was purified by column chromatography on silica gel (CH_2Cl_2/*n*-hexane, 1:1, v/v).
14. All new compounds reported herein showed spectral data consistent with the assigned structures. *Selected data*: compound **7**: Yield: 6.2 mg (0.01 mmol, 21%); mp >300 °C; R_f = 0.52 (CH_2Cl_2/*n*-hexane, 1:1, v/v); ^{1}H NMR (600 MHz, $CDCl_3$): δ −2.68 (s, 2H, N*H*), 1.00 (t, 3H, ^3J = 7.34 Hz, $(CH_2)_4CH_3$), 1.59 (t, 2H, ^3J = 7.70 Hz, $(CH_2)_3CH_2CH_3$), 1.83 (t, 2H, ^3J = 7.70 Hz, $(CH_2)_2CH_2CH_2CH_3$), 2.59 (t, 2H, ^3J = 7.34 Hz, $CH_2CH_2(CH_2)_2CH_3$), 2.73 (s, 3H, $C_6H_4CH_3$), 2.75 (s, 6H, $C_6H_4CH_3$), 5.05 (t, 2H, ^3J = 8.07 Hz, $CH_2(CH_2)_3CH_3$), 7.57 (d, 2H, ^3J = 7.34 Hz, H_{Ar}), 7.59 (d, 4H, ^3J = 7.34 Hz, H_{Ar}), 8.10 (d, 2H, ^3J = 8.07 Hz, H_{Ar}), 8.12 (d, 4H, ^3J = 7.34 Hz, H_{Ar}), 8.83 (s, 4H, H_β), 8.96 (d, 2H, ^3J = 4.40 Hz, H_β), 9.50 (d, 2H, ^3J = 5.14 Hz, H_β) ppm; UV–vis (CH_2Cl_2): λ_{max} (lg ε) = 419 nm (5.7), 517 (4.6), 553 (4.5), 593 (4.4), 649 (4.4); HRMS (ES+) [$C_{46}H_{42}N_4$+H]: calcd 651.3488, found 651.3495. Compound **8**: Yield: 7.8 mg (0.013 mmol, 29%); mp >300 °C; R_f = 0.43 (CH_2Cl_2/*n*-hexane, 1:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ −2.63 (s, 2H, N*H*), 2.72 (s, 3H, $C_6H_4CH_3$), 2.75 (s, 6H, $C_6H_4CH_3$), 4.71 (s, 3H, CH_3), 7.57 (d, 2H, ^3J = 8.03 Hz, H_{Ar}), 7.59 (d, 4H, ^3J = 7.78 Hz, H_{Ar}), 8.10 (d, 2H, ^3J = 7.53 Hz, H_{Ar}), 8.12 (d, 4H, ^3J = 7.78 Hz, H_{Ar}), 8.84 (s, 4H, H_β), 8.96 (d, 2H, ^3J = 4.77 Hz, H_β), 9.53 (d, 2H, ^3J = 4.77 Hz, H_β) ppm; UV–vis (CH_2Cl_2): λ_{max} (lg ε) = 419 nm (5.6), 517 (4.5), 552 (4.4), 593 (4.4), 651 (4.4); HRMS (ES+) [$C_{42}H_{34}N_4$+H]: calcd 595.2862, found 595.2843. Compound **9**: Yield: 21.1 mg (0.033 mmol, 73%); mp >300 °C; R_f = 0.58 (CH_2Cl_2/*n*-hexane, 1:1, v/v); ^{1}H NMR (600 MHz, $CDCl_3$): δ −2.75 (s, 2H, N*H*), 2.72 (s, 3H, $C_6H_4CH_3$), 2.76 (s, 6H, $C_6H_4CH_3$), 3.56 (t, 2H, ^3J = 8.07 Hz, CH_2CN), 5.46 (t, 2H, ^3J = 8.07 Hz, CH_2CH_2CN), 7.58 (d, 2H, ^3J = 8.07 Hz, H_{Ar}), 7.60 (d, 4H, ^3J = 7.34 Hz, H_{Ar}), 8.09 (d, 2H, ^3J = 7.34 Hz, H_{Ar}), 8.11 (d, 4H, ^3J = 8.07 Hz, H_{Ar}), 8.85 (s, 4H, H_β), 9.03 (d, 2H, ^3J = 5.14 Hz, H_β), 9.46 (d, 2H, ^3J = 4.40 Hz, H_β) ppm; UV–vis (CH_2Cl_2): λ_{max} (lg ε) = 419 nm (5.7), 516 (4.6), 551 (4.5), 592 (4.5), 648 (4.4); HRMS (ES+) [$C_{44}H_{35}N_5$+H]: calcd 634.2971, found 634.3000. Compound **10**: Yield: 7.9 mg (0.012 mmol, 26%); mp >300 °C; R_f = 0.26 (ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$): δ −2.77 (s, 2H, N*H*), 1.82 (s, 4H, $NCH_2(CH_2)_2$), 2.72 (s, 3H, $C_6H_4CH_3$), 2.75 (s, 6H, $C_6H_4CH_3$), 2.94 (s, 4H, $NCH_2(CH_2)_2CH_2$), 6.00 (s, 2H, CH_2N), 7.57 (d, 2H, ^3J = 5.87 Hz, H_{Ar}), 7.59 (d, 4H, ^3J = 6.85 Hz, H_{Ar}), 8.10 (d, 2H, ^3J = 4.89 Hz, H_{Ar}), 8.12 (d, 4H, ^3J = 7.83 Hz, H_{Ar}), 8.85 (d, 4H, ^3J = 2.93 Hz, H_β), 8.98 (d, 2H, ^3J = 4.89 Hz, H_β), 9.69 (d, 2H, ^3J = 3.91 Hz, H_β) ppm; UV–vis (CH_2Cl_2): λ_{max} (lg ε) = 421 nm (5.4), 519 (4.3), 554 (4.2), 594 (4.2), 651 (4.1); HRMS (ES+) [$C_{46}H_{41}N_5$+H]: calcd 664.3461, found 664.3440. Compound **11**: Yield: 4.9 mg (0.007 mmol, 16%); mp >300 °C; R_f = 0.28 (CH_2Cl_2/*n*-hexane, 1:1, v/v); ^{1}H NMR (600 MHz, $CDCl_3$): δ −2.72 (s, 2H, N*H*), 2.73 (s, 3H, $C_6H_4CH_3$), 2.75 (s, 6H, $C_6H_4CH_3$), 3.59 (t, 2H, ^3J = 8.44 Hz, $CH_2CH_2OCH_3$), 3.80 (s, 3H, $CH_2CH_2OCH_3$), 5.42 (t, 2H, ^3J = 8.44 Hz, $CH_2CH_2OCH_3$), 7.57 (d, 2H, ^3J = 8.07 Hz, H_{Ar}), 7.59 (d, 4H, ^3J = 7.34 Hz, H_{Ar}), 8.09 (d, 2H, ^3J = 8.80 Hz, H_{Ar}), 8.11 (d, 4H, ^3J = 7.34 Hz, H_{Ar}), 8.84 (s, 4H, H_β), 8.98 (d, 2H, ^3J = 4.40 Hz, H_β), 9.53 (d, 2H, ^3J = 4.40 Hz, H_β) ppm; UV–vis (CH_2Cl_2): λ_{max} (lg ε) = 419 nm (5.6), 516 (4.5), 552 (4.3), 593 (4.2), 651 (4.2); HRMS (ES+) [$C_{45}H_{38}N_4O_2$+H]: calcd 667.3073, found 667.3093. Compound **12**: Yield: 6.7 mg (0.009 mmol, 21%); mp 273 °C; R_f = 0.69 (ethyl acetate); ^{1}H NMR (600 MHz, $CDCl_3$): δ −2.70 (s, 2H, N*H*), 2.73 (s, 5H, $C_6H_4CH_3$, CH_2O), 2.76 (s, 6H, $C_6H_4CH_3$), 2.91 (t, 2H, ^3J = 4.40 Hz, NCH_2), 3.47 (t, 2H, ^3J = 4.77 Hz, OCH_2), 3.57 (t, 2H, ^3J = 8.07 Hz, CH_2CH_2CO), 3.66 (t, 2H, ^3J = 4.40 Hz, CH_2N), 5.47 (t, 2H, ^3J = 9.17 Hz, CH_2CH_2CO), 7.58 (d, 2H, ^3J = 8.80 Hz, H_{Ar}), 7.60 (d, 4H, ^3J = 7.34 Hz, H_{Ar}), 8.10 (d, 2H, ^3J = 4.40 Hz, H_{Ar}), 8.11 (d, 4H, ^3J = 8.07 Hz, H_{Ar}), 8.85 (s, 4H, H_β), 8.99 (d, 2H, ^3J = 4.40 Hz, H_β), 9.53 (d, 2H, ^3J = 4.40 Hz, H_β) ppm; UV–vis (CH_2Cl_2): λ_{max} (lg ε) = 419 nm (5.5), 518 (4.5), 552 (4.4), 592 (4.4), 647 (4.4); HRMS (ES+) [$C_{48}H_{43}N_5O_2$+H]: calcd 722.3495, found 722.3404. Compound **13**: Yield: 24.2 mg (0.034 mmol, 75%); mp >300 °C; R_f = 0.23 (ethyl acetate/*n*-hexane, 1:2, v/v); ^{1}H NMR (600 MHz, $CDCl_3$): δ −2.73 (s, 2H, N*H*), 2.73 (s, 3H, $C_6H_4CH_3$), 2.74 (s, 6H, $C_6H_4CH_3$), 3.72 (s, 3H, NCH_3CH), 3.75 (s, 3H, $CONCH_3CO$), 7.59 (m, 6H, H_{Ar}), 8.00 (s, 1H, *CH*), 8.12 (m, 6H, H_{Ar}), 8.87 (d, 4H, ^3J = 3.67 Hz, H_β), 8.94 (d, 2H, ^3J = 3.67 Hz, H_β), 9.06 (d, 2H, ^3J = 4.40 Hz, H_β) ppm; UV–vis (CH_2Cl_2): λ_{max} (lg ε) = 420 nm (5.8), 516 (4.6), 551 (4.4), 591 (4.3), 648 (4.3); HRMS (ES+) [$C_{47}H_{38}N_6O_2$+H]: calcd 719.3126, found 719.3134.
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17. All new compounds reported herein showed spectral data consistent with the assigned structures. Selected data: compound **14**: Yield: 9.4 mg (0.016 mmol, 35%); mp >300 °C; R_f = 0.22 (CH_2Cl_2/*n*-hexane, 2:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ −2.80 (s, 2H, N*H*), 2.77 (s, 6H, $C_6H_4CH_3$), 3.56 (t, 4H, ^3J = 7.89 Hz, CH_2CN), 5.41 (t, 4H, ^3J = 7.89 Hz, CH_2CH_2CN), 7.61 (d, 4H, ^3J = 7.60 Hz, H_{Ar}), 8.09 (d, 4H, ^3J = 7.60 Hz, H_{Ar}), 9.00 (d, 4H, ^3J = 4.68 Hz, H_β), 9.43 (d, 4H, ^3J = 5.26 Hz, H_β) ppm; UV–vis (CH_2Cl_2): λ_{max} (lg ε) = 418 nm (5.6), 516 (4.4), 551 (4.4), 594 (4.4), 650 (4.4); HRMS (ES+) [$C_{40}H_{32}N_6$+H]: calcd 597.2759, found 597.2767. Compound **15**: Yield: 7.1 mg (0.0115 mmol, 25%); mp 117 °C; R_f = 0.18 (CH_2Cl_2/*n*-hexane, 1:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ −2.73 (s, 2H, N*H*), 0.99 (t, 9H, ^3J = 7.28 Hz, CH_3), 1.45 (m, 6H, $(CH_2)_4CH_2CH_3$), 1.55 (m, 6H, $(CH_2)_3CH_2CH_2CH_3$), 1.84 (m, 6H, $(CH_2)_2CH_2(CH_2)_2CH_3$), 2.53 (m, 6H, $CH_2CH_2(CH_2)_3CH_3$), 3.47 (t, 2H, ^3J = 8.78 Hz, CH_2CN), 4.94 (m, 6H, $CH_2(CH_2)_4CH_3$), 5.32 (t, 2H, ^3J = 8.78 Hz, CH_2CH_2CN), 9.39 (d, 2H, ^3J = 4.77 Hz, H_β), 9.49 (d, 4H, ^3J = 4.77 Hz, H_β), 9.53 (d, 2H, ^3J = 5.02 Hz, H_β) ppm; UV–vis (CH_2Cl_2): λ_{max} (lg ε) = 418 nm (5.6), 518 (4.5), 554 (4.4), 600 (4.3), 656 (4.3); HRMS (ES+) [$C_{41}H_{53}N_5$+H]: calcd 616.4379, found 616.4367. Compound **16**: Yield: 20.2 mg (0.03 mmol, 70%); mp 123 °C; R_f = 0.22 (CH_2Cl_2/*n*-hexane, 1:1, v/v); ^{1}H NMR (400 MHz, $CDCl_3$): δ −2.75 (s, 2H, N*H*), 2.78 (t, 2H, ^3J = 7.31 Hz, CH_2CN), 3.22 (t, 2H, ^3J = 7.60 Hz, CH_2CH_2CN), 7.79 (m, 12H, H_{Ar}), 8.15 (d, 2H, ^3J = 7.02 Hz, H_{Ar}), 8.24 (m, 6H, H_{Ar}), 8.68 (d, 1H, ^3J = 4.68 Hz, H_β), 8.71 (s, 1H, H_β), 8.81 (d, 1H, ^3J = 4.68 Hz, H_β), 8.83 (d, 1H,

^3J = 4.68 Hz, H_β), 8.87 (m, 3H, H_β) ppm; UV–vis (CH_2Cl_2): λ_{max} (lg ε) = 419 nm (5.4), 516 (4.2), 551 (4.0), 591 (3.9), 648 (3.9); HRMS (ES+) [$C_{47}H_{33}N_5$+H]: calcd 668.2814, found 668.2836.

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