Electrochemical Synthesis of Hetero[7]helicenes, Dehydro-hetero[7]helicenes and Hetero[8]circulenes with Intriguing Optical Features

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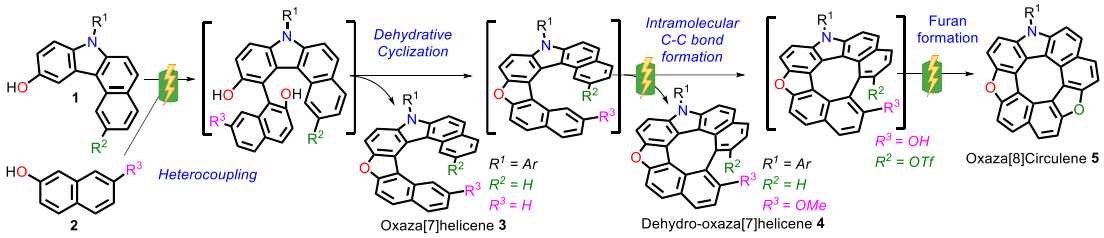
Polycyclic heteroaromatic compounds (PHAs) including helicenes, dehydrohelicenes, and circulenes show unique architectures that endowed them with various desirable optical and electronic features. Although various successful strategies were introduced to afford PHAs, there are some remaining limitations related to the low total yields, harsh reaction conditions (such as high temperature), easy racemization of the synthetic intermediates, and/or overuse of oxidants (narrow functional group tolerance).[1]

In this work, we introduce the first electrochemical approach for synthesizing unsymmetrical PHAs *via* sequential transformations. The electrochemical sequence starts with the chemoselective hetero-coupling of 3-hydoxycarbazoles **1** and 2-naphthols **2**, followed by a dehydrative cyclization to afford oxaza[7]helicenes **3**.[2] We extended our protocol by re-optimizing the electrochemical parameters and varying substrate **2** to include an additional step; the intramolecular carbon-carbon bond formation giving dehydro-oxaza[7]helicenes **4**.[3] Hetero[8]circulenes **5** were prepared in good yields *via* a four-step sequence that involved the dehydrative furan formation as the final step. The chiral stability and optical features of these PHAs were studied and revealed interesting characteristics. An intense blue-colored circularly polarized luminescence CPL with $|g_{lum}| = 2.5 \times 10^{-3}$ at 433 nm was observed which is the highest among reported dehydrohelicenes.[3]



References

1) A. Borissov, Y.K. Maurya, L. Moshniaha, W.-S. Wong, M. Żyła-Karwowska, M. Stepien, *Chem Rev.* **2021**, *122*, 565. 2) a) M.S.H. Salem, M.I. Khalid, M. Sako, K. Higashida, C. Lacroix, M. Kondo, R. Takishima, T. Taniguchi, M. Miura, G. Vo-Thanh, H. Sasai, S. Takizawa, *Under Review;* b) M.S.H. Salem, A. Sabri, M.I. Khalid, H. Sasai, S. Takizawa, *Molecules* **2022**, *27*, 9068. 3) M.I. Khalid, M.S.H. Salem, M. Sako, M. Kondo, H. Sasai, S. Takizawa, *Commun. Chem.* **2022**, *5*, 166.