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Deuteration of molecules for neutron reflectometry on organic light-emitting diode thin films

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ABSTRACT

Deuterated forms of aromatic charge transporting heterocycles **2** and **3** used in organic light-emitting diodes have been produced by hydrothermal reactions, catalyzed by Pt/C or Pd/C. Comprehensive analysis by mass spectroscopy, ^{1}H, ^{2}H and ^{13}C NMR enables determination of the overall quantity of D atoms present, as well as the level of deuteration at each molecular site. The roles of solubility and steric availability in deuteration are discussed in the light of these results. Neutron reflectometry indicates excellent scattering contrast between protonated and deuterated forms of these molecules, with nanoscale thin films showing the same density as in their bulk molecular forms. Although used for morphological studies of thin films typically used in OLEDs, the synthetic and analysis methods described here are generic and suitable for deuteration of other conjugated aromatic heterocycles and other optoelectronic devices.

Organic optoelectronics is a rapidly growing area of interdisciplinary science and technology, with investigations focused on both small molecules,[1,2] conjugated polymers,[3a] and dendrimers[3b,c] that can be used as the light-emitting layers in organic light-emitting diodes (OLEDs). A fundamental feature of these devices is that they are comprised of more than one layer and hence rely on electron transfer processes at interfaces. Conjugated aromatic heterocycles such as **2** and **3** (Fig. 1) are widely used electron and hole transport materials, respectively. The current generation of OLEDs, having internal quantum efficiencies of ~100%, are based on small molecule phosphorescent iridium(III) complexes [e.g., *fac*-tris(2-phenylpyridyl)iridium(III) ($Ir(ppy)_3$] blended with an organic host material [e.g., 4,4′-bis(*N*-carbazolyl)biphenyl (CBP)] in the emissive layer.[2] While efficiencies of these layered devices are very high, their lifetimes depend on a range of factors including the morphological stability of layers in the device.[4] Investigations of functioning devices with buried interfaces present numerous difficulties using conventional surface science techniques and so neutron reflectometry along with selective deuteration has become the key method for the study of morphology, diffusion, and interfacial behavior in organic thin-film semiconducting devices.[5] Selective deuteration of these aromatic and heterocyclic molecules leads to a substantial increase in neutron scattering length density compared to their equivalent protonated forms. In addition to such morphological studies, recent investigations have also centered on isotope effects associated with deuterium that lead to substantial increases in the quantum efficiency and high-voltage stability of Al-based[5j] and Ir-based[5k] OLEDs.

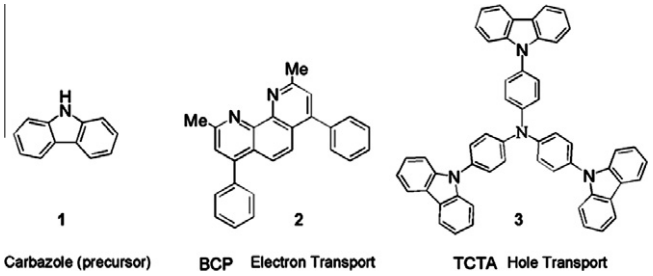

Figure 1. OLED molecules **2** and **3** and precursor **1**.

There have been a number of studies detailing different methods for synthesizing deuterated aromatic and heterocyclic compounds; these being ably summarized by the early work of Hawthorne et al.[6] and recent published works of Derdau, Atzrodt, and co-workers,[7] as well as numerous studies by Sajiki et al.[8] This Letter reports the deuteration of molecules that form key components of the electron and

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hole transport layers of an OLED device, and assesses the synthetic outcomes in light of different deuteration conditions. The role of solubility and steric availability of proton sites is also discussed. Finally, results from the application of these deuterated molecules in the study of interfacial morphology of films typically applied in OLEDs using neutron reflectometry are presented.

Deuteration of the molecules presented in this study was achieved either by H/D exchange reactions with deuterium oxide catalyzed by Pt/C and Pd/C under hydrothermal conditions, or by synthesis from deuterated precursors produced by the same method. Sajiki et al. have demonstrated that platinum catalysts generally have a higher tendency toward the deuteration of aromatic positions, whereas palladium catalysts preferentially deuterate aliphatic positions.[8i] The same authors also showed that Pt/C and Pd/C when used together have a synergistic effect in deuterating sterically hindered aromatic positions.[8j] It is known that this method is dependent on both electronic and steric factors, and it has been suggested that the high affinity of Pt or Pd metal for a nitrogen lone pair increases the efficiency of the exchange reaction.[8e] Lower incorporation of deuterium has been observed on groups neighboring sterically encumbered nitrogen atoms. For our study, the optimized conditions, overall yield and deuteration outcomes are summarized in Table 1.

Carbazole-d_8 (**1**) was the most efficiently produced molecule in this study under hydrothermal conditions (240 °C), which was performed on ca. 10 g scale and gave 80% yield and 94% deuteration of the aromatic proton sites (Supplementary data, Figs. S1–S3). This is attributed to the high solubility of carbazole in D_2O at elevated temperatures and the lack of steric crowding of its proton sites.

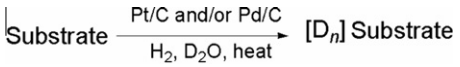
Although prepared at a lower temperature (180 °C) than **1**, the optimized hydrothermal deuteration of BCP-d_{20} (**2**) gave a poorer yield (50%) and lower deuteration levels. The broad isotope cluster shown in the ESI-MS spectrum of BCP-d_{20} (Fig. 2) indicates a distribution of protonated and deuterated sites within the molecule (incomplete deuteration). The analysis of the area under these peaks in the spectrum suggests an average of 68% deuteration. The presence of the signal m/z: 361, which corresponds to the completely non-deuterated species (i.e., d_0), separate from the continuous isotope cluster (d_{11}–d_{20}) suggests solubility issues. Material that remained insoluble is expected to stay non-deuterated, while the material that dissolved in the solution incorporated deuterium atoms and formed a continuous mass distribution envelope (d_{11}–d_{20}). The combination of ^{1}H, ^{2}H and ^{13}C NMR spectra (Supplementary data, Figs. S4–S8) allowed us to confirm the total deuterium content for this molecule, but also importantly, gives a clear indication of the relative occurrence of hydrogen and deuterium atoms at specific sites within the molecule.

The percentage protonation of residual signals for individual ^{1}H resonances within the molecule was determined by ^{1}H NMR spectroscopy (Supplementary data, Fig. S4) using a protonated internal standard (i.e., MeOH). ^{2}H NMR spectroscopy confirmed the deuteration at these positions by showing reciprocal resonances for each deuterated position (Supplementary data, Fig. S5), whereas ^{13}C NMR spectroscopy allowed observation of the deuterated and protonated extent at each position simultaneously, utilizing the secondary isotope effect on the observed ^{13}C nucleus.[9] The latter was achieved by running an inverse gated ^{13}C NMR experiment with long delays between pulses (i.e., D_1 = 20 s); observing ^{13}C nuclei while decoupling both ^{1}H and ^{2}H nuclei. This technique is a particularly useful analysis tool, as experiments can be designed that discriminate between resonances of the various types of carbons present: fully deuterated groups (CD, CD_2, CD_3), partially deuterated groups (CHD, CHD_2, CH_2D), and non-deuterated groups (C, CH, CH_2, CH_3). By comparing the ^{13}C{^{1}H, ^{2}H} (decoupling both ^{1}H and ^{2}H) spectrum to the normal ^{13}C{^{1}H} (proton decoupled only) NMR, it was possible to differentiate between carbons with and without deuterons. This allowed the determination of the percent deuteration at specific sites in the molecule, as shown in Figure 3, and confirmed the percent deuteration obtained from ^{1}H NMR analysis with an internal standard, the values agreeing to within ±1%. Additionally, this technique allowed determination of the percent deuteration at carbon positions where the corresponding residual proton resonances overlap in the ^{1}H NMR spectrum. For example, in BCP (2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline), the residual protons at the *ortho*, *meta*, and *para* positions of the two phenyl groups at position C(3) (Fig. 3) have overlapping resonances in the ^{1}H NMR spectrum, while their three carbon resonances in the ^{13}C NMR spectra are well resolved (Supplementary data, Fig. S8).

Of the 20 protons available within BCP, six distinct sites are evident (Fig. 3) which were found to be deuterated to different degrees depending on the steric hindrance and availability of these sites for H/D exchange with the catalyst. Methyl protons at the C(1) position showed the highest deuteration levels (90%), while protons at the C(2) position showed only 40% deuteration due to the steric shielding from the phenyl groups. The *ortho*-, *meta*-, and *para*-positions on the two phenyl groups at position C(3) in Figure 3 were found to be deuterated at 55%, 86%, and 90%, respectively. The remaining two protons attached to the phenanthroline moiety at position C(4) are strongly sterically shielded by the pendant phenyl groups, such that the catalyst had restricted access to these positions and hence they were deuterated at the 4% level.

Attempts at producing TCTA-d_{36} [tris(4-carbazoyl-9-ylphenyl)amine-d_{36}] using hydrothermal methods and a similar approach to that used for **1** produced either no deuteration at 240 °C, or substantial decomposition (30% yield) and poor deuteration (15% D) at 265 °C (Supplementary data, Fig. S9). The lack of deuteration at lower temperatures appears to be correlated to the poor solubility of TCTA in D_2O.

Table 1
Optimized hydrothermal reaction conditions for **1**–**3**



Reagents/catalyst	Temp. (°C)	Time (h)	Composition/average % deuteration	Yield (%)
Carbazole (59.8 mmol), D_2O (120 mL), Pt/C (2.5 g)	240	48	$C_{12}D_8HN$ (**1**) 94%	80
BCP (1.38 mmol), D_2O (35 mL), Pt/C (0.25 g)	180	96	$C_{26}D_{14}H_6N_2$ (**2**) 68%	50
TCTA (0.67 mmol), D_2O (30 mL), THF (10 mL), Pt/C (0.23 g), Pd/C (0.23 g), H_2 (1 L)	140	18 × 3[a]	$C_{54}D_{15}H_{21}N_4$ (**3**) 42%	56

[a] Products were extracted and analyzed after each run, before returning to the Parr reactor with fresh reagents and catalysts.