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# **Doubly Bridged Anthracenes: Blue Emitters for OLEDs**

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The photooxidative stability of a series of doubly bridged anthracenes was evaluated after their preparation *via* twofold macrocyclization of a bis(resorcinyl)anthracene. Lightfastness correlates with the energy levels of the highest occupied molecular orbital (HOMO), resulting in superior stability of the tetraesters compared to the tetraethers. The lengths and steric

## Introduction

Anthracenes are widely used and easily synthesized emitters in organic light-emitting diodes (OLEDs).<sup>[1-11]</sup> They are processable both from solution<sup>[12]</sup> or *via* vacuum deposition,<sup>[5]</sup> and exhibit (deep-)blue emission with quantum yields ( $\Phi$ ) approaching unity.<sup>[13-15]</sup> This is a prerequisite to achieving high external quantum efficiencies, as only 25% of all excitons in devices based on conventional fluorophores can be harvested.<sup>[16,17]</sup> For example, 9,10-diphenylanthracene 1 (Figure 1,  $\Phi = 97\%$  in *n*-hexane and 68% in thin-films)<sup>[14]</sup> fluoresces in the deep blue regime. Stable deep blue emitters are one of the bottlenecks in OLED technology.<sup>[9,18-20]</sup>

To improve the stability of anthracenes, their decomposition reactions need to be slowed: Depending on their substituents, anthracenes may undergo photoinduced [4+4] cycloadditions, forming dimers,<sup>[21]</sup> or photooxidation yielding their 9,10-*endo*-peroxides with follow-up reactions,<sup>[22,23]</sup> both at the vulnerable 9,10-positions. Degradation of anthracenes is decelerated/

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demand of the linker only plays a minor role for the ester-based compounds, which can be prepared in reasonable yields and thus tested in proof-of-concept organic light-emitting diodes. Double ester-bridging allows deep blue electro-luminescence, highlighting the importance of the choice of the functional groups used for macrocyclization.



**Figure 1.** Anthracene-based blue emitters and their half-lives  $t_{1/2}$  in dichloromethane; irradiation with a handheld UV-lamp ( $\lambda_1 = 254$  nm and  $\lambda_2 = 365$  nm) under ambient conditions.<sup>[31,32]</sup> Red numbers exemplify determination of bridge size in **3**.

impeded by their non-covalent encapsulation in self-assembled complexes<sup>[24,25]</sup> or proteins via host guest chemistry;<sup>[26]</sup> within rotaxanes<sup>[27]</sup> or through attachment of sterically demanding substituents, for example triisopropylsilyl(TIPS)-ethynyls in 2.[23] A unique case is the covalent embedding of anthracenes into macrocycles. Gidron's anthrylene-based cyclophanes mainly serve to exert strain onto the aromatic backbone;<sup>[28,29]</sup> whereas Kobayashi et al. improved the stability of anthracene via double alkylene-bridging in **3**.<sup>[14]</sup> Although the  $\pi$ -system is well-shielded in these bicyclophanes, the resorcinyl substituents render these emitters more electron-rich, facilitating oxidation by increasing the ionization potential (IP).<sup>[30]</sup> Recently, Müllen et al. and Höger et al. presented the most stable anthracene-based emitter to date.<sup>[31,32]</sup> In **4**, the anthracene is embedded in the center of a [6]cyclo-meta-phenylene. Compared to 3, the half-life of 4 (irradiation in dichloromethane, air) increased by a factor of 27, testimony to a higher oxidation potential, as well as improved shielding of the anthracene core.<sup>[31]</sup> One major drawback is the difficult synthesis of 4 - the condensation of the pyrylium salt with anthrylenediacetic acid as the limiting step. Batch sizes are small and yields only reach 13%.[32] Thus, systems as easily synthesized as 3 with a stabilizing effect as large as in 4 are attractive targets.

Here, we synthesized anthracene-based bicyclophanes, investigated their photostability in dilute solutions, selected the

lightfastest derivatives and incorporated them into bluefluorescent OLEDs. Starting from Kobayashi's alkylene-bridged **3**, we investigated the size and nature of the alkylene bridges (**8**: reduction of tether size; **6**, **7**: glycole-based bridges instead of alkylene linkers), and the influence of the functional groups attaching the bridges to the phenyl rings to reduce sensitivity towards oxidation (**9–12**: carboxylates instead of ethers). Last, we also elucidated the influence of regioisomerism on the stability by attaching the macrocycle at the 1,5- instead of the 9,10-positions (c.f. **17**).

## **Results and Discussion**

### Synthesis

For 9,10-substituted anthrylenes, tetraol **5** was prepared from anthraquinone on the gram scale (see Supporting Information, Scheme S1).<sup>[14]</sup> The photostability of bridged acenes strongly depends on the length of the bridge in between the phenyl substituents,<sup>[14,33]</sup> but the influence of the nature of the bridges has not yet been investigated. Employing Kobayashi's protocol, we synthesized alkylene- and ethylene glycol bridged **6–8** after treatment of **5** with potassium carbonate in DMF in the presence of  $\alpha$ , $\omega$ -dihalides (Scheme 1). Bridge sizes amount to 10



(6) and 7 (7, 8) – as expected, yields increase with the length of the tethers.

To vary the electronics, ester instead of ether linkages were introduced into bicyclophanes **9–12** by reacting **5** with commercially available bisacid chlorides. Adopting procedures of Bunz *et al.*<sup>[34]</sup> and Böhmer *et al.*,<sup>[35]</sup> macrocyclization was optimized for the generation of **11**. At low concentration  $(4.2 \times 10^{-3} \text{ M})$ , pimeloyl chloride was slowly added to a solution of **5** in boiling THF and triethylamine (8 h) furnishing **11** in 32% yield. Increasing the size of the bridge from 9 to 10 improved yield to 52% for **12**, whereas a decrease by one yielded only traces of **10**. The eight-membered bridge is too short for the ring closing reaction to occur efficiently at the carbonyl center. To implement a bulkier bridging fragment, adamantylenediacetic acid chloride was reacted with tetraol **5**, furnishing the adamantylene-bridged anthracene **9** in 32% yield.

Simple molecular mechanics models (see Supporting Information, Figure S41) suggested that by varying the substitution pattern from 9,10 to 1,5, a larger portion of the anthracene  $\pi$ -system is physically blocked with diagonal alkylene bridges. Suzuki coupling of 1,5-dibromoanthracene **13**<sup>[36]</sup> with 2,6-dimethoxyphenylboronic acid followed by deprotection with BBr<sub>3</sub> yielded tetraol **15**. Bridging furnished alkylene-bridged **17** (yield: 5%) with a bridge size of 9. For reference, its consanguine TIPS-ethynylated analogue **16** was synthesized *via* Stille coupling in 63% yield (Scheme 2).

#### Single crystal structures

Single crystals suitable for X-ray analysis were obtained by diffusion of antisolvents into chloroform solutions (see Figure 2 and Supporting Information, Figure S46). Bridging generally increases the torsion of the phenyl substituents from  $65^{\circ}$  (1),



**Scheme 1.** Synthesis of doubly bridged anthracenes. i)  $K_2CO_3$ , DMF, 40 °C to 80 °C, 3 d; ii) NEt<sub>3</sub>, THF, reflux, 8 h. Red numbers in parentheses denote the bridge size.

**Scheme 2.** Synthesis of doubly bridged anthracene **17** and its consanguine silylethynylated counterpart **16**. i)  $K_2CO_3$ ,  $Pd_2(dba)_3$ , SPhos, toluene, water, 95 °C, 72 h; ii) PdCl\_2(PPh\_3)\_2, THF, 70 °C, 16 h; iii) DCM, r.t., 96 h; iv)  $K_2CO_3$ , DMF, 40 °C to 80 °C, 3 d. The red number in parentheses denotes the bridge size.

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either slightly (6, 11) or to values as large as  $88^{\circ}$  (12) with respect to the anthracene core (Supporting Information, Table S2). No obvious correlation between bridge size and torsion angle is found – torsion angles are most likely a consequence of intermolecular crystal packing effects.

In **8**, with the shortest (bridge size of 7) and most rigid bridge (c.f. top view in Figure 2), the central methylene unit of the pentylene bridge hovers 3.2 Å above the central anthracene ring. As a consequence, it is shielded in the proton NMR spectrum ( $\delta = -0.6$  ppm). Similarly, for **17** and **9**, upfield shifts as low as  $\delta = -0.3$  ppm and -0.1 ppm are observed due to proximity of the bridges to the aromatic core, as reflected in the front-views of their crystal structures.

Both the adamantylene (in **9**) and the diagonal alkylene bridge (in **17**) with a bridge size of 9 improve shielding/ coverage of the aromatic system compared to **11**, whose flexible 9-membered linker adopts a S-shaped conformation (top-view). The packing of the bridged anthracenes is dominated by van-der-Waals interactions of the bridges – the chromophores are isolated (see Supporting Information, Fig-



Figure 2. Solid state structures of bridged anthracenes 8, 11, 9, 17. Top: stick model. Mid: top-view of space-filling models. Bottom: front-view of space-filling models.



Figure 3. Packing of 10 in the single crystal. Hydrogen atoms in close contact with the carbonyl function are shown as spheres. All other hydrogen atoms were omitted for clarity.

ure S47). The exception is **10**, which exhibits small  $\pi$ - $\pi$  interactions (distance: 3.46 Å) between the anthracene cores as it forms declined one-dimensional stacks with C=O<sup>...</sup>H-C<sub>sp2</sub> short contacts in the single crystal (Figure 3).

#### **Optoelectronic properties**

The encapsulated anthracenes are colorless solids, whereas the TIPS-ethynyl substituted ones appear yellow. The blue fluorescent materials are well soluble in chlorinated and polar aprotic solvents. Absorption spectra (Figure 4a and Supporting Information, Figure S25 and Figure S26) display the characteristic vibronic finger structure (p-bands) at long wavelengths. The absorption profiles do not differ significantly for the encapsulated derivatives - they are independent of the functional group due to the almost orthogonal orientation of the phenyl substituents. The absorption maxima range between 400 nm (9, adamantylene bridge) and 387 nm (17, diagonally bridged). Shorter, more rigid systems absorb red-shifted (7-9;  $\lambda_{max} \ge$ 396 nm) compared to the longer ones (12, 6;  $\lambda_{max}$  = 392 nm and 393 nm, respectively). TIPS-ethynylated 2 and 16 are most redshifted due to their extended conjugated  $\pi$ -systems. The trend in absorption (and emission, see below) maxima is mirrored in the calculated gaps (~3.4 eV for bridged anthracenes, Table 2 and Supporting Information, Table S1). TIPSethynylation stabilizes the LUMO energy levels - this effect is more pronounced in 9,10- (2) than in 1,5-position (16).



**Figure 4.** a) Normalized absorption (black line) and emission spectra (blue line) of TIPS-ethynylated anthracene **2** and bridged anthracene **11** in *n*-hexane. b) CIE coordinates of the standard blue points recommended by the National Television System Committee (NTSC) and the European Broadcast Union (EBU)<sup>[37]</sup> together with the anthracenes in the CIE chromaticity diagram.<sup>[38]</sup>

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Table 1. Optical properties of bridged anthracenes and their consanguine           TIPS-ethynylated counterparts in solution ( <i>n</i> -hexane).										
Compd	λ <sub>max, abs</sub> [nm]	λ <sub>onset, abs</sub> [nm]	λ <sub>max, em</sub> [nm]	$arDelta ilde{ u}$ [cm <sup>-1</sup> ]	Ф [%]	E <sub>gap</sub> [eV] <sup>[a]</sup>				
1	392	405	406	880	77	3.06				
2	437	446	440	156	76	2.78				
3	393	406	403	631	74	3.05				
6	393	406	401	508	25	3.05				
7	396	408	402	377	52	3.04				
8	397	407	402	313	50	3.05				
9	400	410	407	430	78	3.02				
11	394	406	405	689	83	3.05				
12	392	406	405	819	79	3.05				
16	411	421	416	292	18	2.94				
17	387	399	396	587	32	3.11				

All emission spectra are mirror images of the respective anthracene p-bands. Stokes shifts correlate with the rigidity of the respective systems: They are smallest for the TIPS-ethyny-lated anthracenes (**2**: 292, **16**: 156 cm<sup>-1</sup>), and increase with the size of the bridges (313 cm<sup>-1</sup> for 7-membered **8** and 819 cm<sup>-1</sup> for 10-membered **12**, almost as high as 880 cm<sup>-1</sup> for DPA **1**).

The anthracenes emit in the desired deep-blue<sup>[9,19]</sup> region with a CIE<sub>y</sub> < 0.1 (Figure 4b). Bridged anthracenes ( $\lambda_{max,em}$ = 396 nm to 407 nm) show similar CIE coordinates as diphenylan-thracene 1, while the TIPS-ethynylated 16 and especially 2 ( $\lambda_{max,em}$ =416 nm and 440 nm, respectively) are shifted to lower CIE<sub>x</sub> and higher CIE<sub>y</sub> values.

Introduction of the ester groups results in quantum yields (in *n*-hexane) as high as 78–83% for **9**, **11**, **12**. They are independent of the length of the bridges and comparable to those of reference emitters DPA **1** (77%) and **3** (74%).<sup>[39]</sup> A reduction of the alkylene bridge (from 9 to 7 members) in **8** or oxygen-incorporated **7** reduces QYs to 50% or 52%, respectively. Varying the substitution pattern from 9,10- (**3**) to 1,5position (**17**) while maintaining the length of the bridge significantly decreases  $\Phi$  to 32%. This trend is also observed for the TIPS-ethynylated species **2** and **16**.

Table 2 compares electro- and quantum-chemical data of 1-3 and 11 (see Supporting Information, Table S1 for guantumchemical data of 6-9, 12, 16, 17). Only 2 displays a reduction event  $(-1.97 \text{ V vs. Fc/Fc}^+)$  within the electrochemical window (cyclic voltammetry, dichloromethane), testimony to its electron-withdrawing TIPS-ethynyl substituents, lowering the electron affinity (EA). Replacement of ether (3) with ester linkages (11) decreases both FMO energy levels by roughly 0.3 eV. Experimentally, 11 is harder to (reversibly) oxidize by 0.26 V. Due to their electron-deficient nature we expect the esterbridged derivatives to be more resistant with respect to (photo)oxidation. Despite 2 and 11 displaying similar HOMO levels (-5.44 eV/-5.48 eV), 2 is significantly easier oxidized  $(\Delta E_{1/2}^{ox} = 0.17 \text{ V})$ . The discrepancy between CV-derived IP/EA and quantum-chemical FMO levels is related to i) the torsion-angle dependence of the FMO levels (see Supporting Information, Figure S42) and, more importantly, ii) the steric shielding of the redox-active chromophore impeding electron transfer to/from the electrodes. This was also observed for sterically shielded pentacenes<sup>[43]</sup> and is most likely the cause as to why the recording of CV spectra of the remaining shielded anthracenes was unsuccessful. The reduced steric shielding in 1 and 2 diminishes discrepancies in the CV experiment matching theoretical differences (HOMO levels: 1: -5.42 eV, 2: -5.44 eV; IP: 1: -5.86 eV, 2: -5.90 eV).

### Lightfastness

To assess the relative stabilities of the chromophores, the timedependent absorption decays were monitored at the absorption maximum while irradiating dichloromethane solutions ( $c = 10^{-5}$  M, quartz cuvettes) with a hand-held UV lamp ( $\lambda_1 = 254$  nm,  $\lambda_2 = 365$  nm, distance to cuvette: 20 cm) under air. Note that in contrast to TIPS-ethynylated **2** and **16**, the degradation of bridged anthracenes yielded decomposition products absorbing at longer wavelengths than  $\lambda_{max}$ , albeit with lower intensities over the course of 48 h (see Supporting Information, Figure S28). This is why the initial evolution over 2.5 h is evaluated (Table 3 and Figure 5).

The resistance to photooxidation in DCM increases in the following sequence:  $6 < 3 \ll 17 \approx 7 \approx 2 \ll 16 < 8 < 12 \approx 9 \approx 11$ . Three groups are discernible: Ether-bridged 3 and glycol-

counterpart 2.	mical data (CV meas	ured in DCM) and ca	alculated FMOs of	I, the bridged anth	racenes 3, 11 and	their consanguine I	IPS-ethynylatec
Compd	E <sup>ox</sup> <sub>1/2</sub> [V]	E <sup>red</sup> <sub>1/2</sub> [V]	IP [eV] <sup>[a]</sup>	EA [eV] <sup>[a]</sup>	E <sub>HOMO</sub> [eV] <sup>[b]</sup>	E <sub>LUMO</sub> [eV] <sup>[b]</sup>	$E_{gap}$ [eV] <sup>[b]</sup>
1	0.76	-	-5.86	-	-5.42	-2.00	3.42
2	0.80 (0.8) <sup>[c]</sup>	-1.97 (-1.9) <sup>[c]</sup>	-5.90	-3.13	-5.44	-2.53	2.91
3	0.71	-	-5.81	-	-5.25	-1.81	3.44
11	0.97	_	-6.07	-	-5.48	-2.09	3.39

[a] IP =  $-e(5.10 V + E_{1/2}^{ox1})$ , EA =  $-e(5.10 V + E_{1/2}^{red})$ .<sup>(41]</sup> [b] Obtained from DFT calculations (Gaussian16<sup>[40]</sup> B3LYP/def2-SVP//Gaussian16 B3LYP/ def2-TZVP; TMS groups were used instead of TIPS). [c] Values from reference.<sup>[42]</sup>

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10

24

bridge size

*l/l*<sub>0</sub> [%] (2.5 h)

7

48

52



9

86

5	1 5		0							
Table 3. Intensity	able 3. Intensity ratio at $\lambda_{abs, max}$ for bridged anthracenes 3, 6–9, 11, 12, 17 and their silylethynylated counterparts 2 and 16 after irradiation with a									
handheld UV lam	p ( $\lambda_1 = 356 \text{ nm}$	and $\lambda_2 = 254$	nm) in dichloro	methane at	room temper	ature under an	nbient condi	tions for 2.5 h.		
Compd	6	3	17	7	2	16	8	12	9	11

65

7

74



9

30

9

47

Figure 5. Time dependent evolution (first 2.5 h) of UV-Vis absorption intensities at  $\lambda_{abs,max}$  for bridged anthracenes 3, 6–9, 11, 12, 17 and TIPSethynylated analogues 2 and 16 under irradiation with a handheld UV lamp ( $\lambda_1 = 356$  nm and  $\lambda_2 = 254$  nm) in dichloromethane at room temperature under air.

bridged 6 decompose fastest. Their bridge sizes of 9 and 10 are longer than that of glycol-bridged 7 (bridge size: 7), forming the next cluster together with 9,10-TIPS-ethynylated 2 and diagonally-bridged 17 (bridge size: 9). The last group consists ofTIPS-ethynylated 16, which is slightly less stable than etherbridged 8. As expected, ester-functionalized 9, 11, 12 are most stable - they are three times as stable as Kobayashi's 3 under these conditions and twice as reluctant to decompose as silylated 2. Stability studies under N<sub>2</sub> instead of air gave similar half-lives and trends (see Supporting Information, Figure S34), concluding that oxidation is not a predominant decomposition pathway for these derivatives.

We note: i) Shorter ether bridges increase stability (8 > 3). ii) Incorporation of oxygen into the ether bridges ("glycols") decreases lightfastness. iii) TIPS-ethynyl groups stabilize better when placed in 1,5-position. iv) Stability of the ester-functionalized anthracenes is quasi-independent of the nature (adamantylene vs. alkylene) and length of the bridges and most likely a consequence of the electron-withdrawing nature of the functional group. Overall, the lightfastness of the anthracenes correlates with the energy level of the HOMO (see Supporting Information, Figure S43).

#### Organic light-emitting diodes (OLEDs)

We now evaluated the behavior of anthracene-bridged derivatives in optoelectronic devices. The three most stable esterfunctionalized molecules 9, 11 and 12 were employed as active materials in OLEDs and compared to the Kobayashi reference

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material 3. The four selected molecules are displayed in Figure 6.

10

80

9

82

To obtain a complete picture of the electronic properties of the materials, the absolute positions of the HOMO and Fermi level (FL) were determined. LUMO levels were estimated by adding the values of HOMO level and optical gap  $E_{opty}$ determined from the absorption and emission spectra (Supporting Information, Figure S49). Ultraviolet photoelectron spectroscopy (UPS) was performed on thin films (deposited on conductive substrates to avoid charging effects). The Fermi level corresponds to the secondary electron cutoff and the HOMO level is determined by the onset in the valence band region of the UPS spectra (shown in Figure S53 of the Supporting Information).

All four anthracene derivatives (Table 4) display similar values for HOMO and LUMO, as predicted by their location on the anthracene core in the DFT calculations discussed earlier.

Having determined the suitability of the materials as blue emitters, we investigated the efficiency of the emission by photoluminescence quantum yield (PLQY). Anthracene-based emitters can form excimers resulting in emission quenching.<sup>[4,44-46]</sup> This is confirmed by the pristine materials showing only moderate quantum yields for neat films, spin coated from chloroform solutions, reaching PLQY values of 31% (3), 25% (9), 23% (11) and 25% (12). To reduce aggregation,<sup>[44,47]</sup> we used host material CBP (4,4'-bis(N-carba-



Figure 6. Bridged anthracenes 3, 9, 11, 12 employed as active emitter layer in OLEDs.

Table 4. Summary of obtained energy levels for the four employed molecules in thin films.							
Compd	$E_{\rm opt}  [eV]^{[a]}$	FL [eV] <sup>[b]</sup>	$E_{\text{HOMO}}  [\text{eV}]^{[\text{b}]}$	$E_{\text{LUMO}} [eV]^{[c]}$			
3	3.0	-4.7	-5.7	-2.7			
9	3.0	-4.8	-5.9	-2.9			
11	3.1	-4.9	-5.9	-2.8			
12	3.1	-4.9	-5.9	-2.8			
[a] Determined from the intersection of the absorption and emission spectra of thin films. [b] From UPS measurements. [c] $E_{LUMO} = E_{HOMO} + E_{opt}$ .							



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zolyl)-1,1'-biphenyl) due to its advantageous HOMO / LUMO energy levels (-6.0 eV / -2.9 eV, respectively).<sup>[48]</sup>

Upon stepwise increase of the ratio of emitter to host between 1% and 10%, we found that a ratio of 5% emitter in CBP yielded the most homogenous films without phase separation. Quantum yields improved to 52% (**3**), 51% (**9**), 41% (**11**) and 28% (**12**). It should be noted that a CBP-only film shows a low PLQY of 2.5%, not contributing to the PLQY increase of the materials.

OLED stacks consisted of ITO/PEDOT:PSS/emitter (5% in CBP)/Ca/AI – characteristic curves of current density vs. voltage (*JV*) and luminance vs. voltage (*LV*) were measured.

The JV characteristics shown in the top panel of Figure 7 are similar for all four molecules. The devices display leakage current below 4 V. The current density increases at 4 V, however there is no increase in luminance (see bottom panel). The current density again increases above 10 V. At this point there is an increase in luminance, indicating increased charge carrier recombination.



**Figure 7.** Current density/voltage/luminance (JVL) characterization of OLEDs fabricated for each of the four molecules with the CBP host matrix.



Figure 8. a) The spectral emission of OLEDs including molecules 9, 11 and 12 are similar and are mainly dominated by peaks at 408 nm and 430 nm. An OLED with molecule 3 displays a large contribution centered at 550 nm. b) The calculated CIE coordinates demonstrate that 9, 11 and 12 are perceived as deep blue while molecule 3 is perceived as white.

The turn-on voltages (defined as the voltage at which the luminance signal rises from the noise) are 10 V for **3**, 9 V for **9**, 8 V for **11** and 9 V for **12**, yielding OLEDs with maximum luminance of 136 cd m<sup>-2</sup> for **3**, 73 cd m<sup>-2</sup> for **9**, followed by 27 cd m<sup>-2</sup> and 22 cd m<sup>-2</sup> for **12** and **11**, respectively. An OLED with the beforementioned stack and 9,10-diphenylanthracene **1** as the emitter was also constructed and achieved a maximum luminance of 51 cd m<sup>-2</sup>.

The spectra of the light emitted by the OLEDs was evaluated by electroluminescence (EL) measurements (Figure 8a). All four molecules display two emission peaks, one at 408 nm and one at 430 nm, identical to the PL spectra. However, **3** has an additional broad emission above 540 nm probably due to excimers.<sup>[45]</sup>

Finally, the perceived color of the devices incorporating the four molecules is shown in the form of CIE coordinates (*x*, *y*) in Figure 8b. For **3**, due to the broad additional emission seen in the EL spectrum, the CIE coordinates (0.26, 0.28) are shifted towards white. In contrast, the ester-containing anthracene derivatives **9**, **11** and **12** emit in the deep blue region with x values of 0.17 and y values <0.1, close to the NTSC-recommended blue point for full-color displays at CIE coordinates (0.14, 0.08),<sup>[49]</sup> and show successful implementation of our bridged anthracene molecules in blue OLEDs.

## Conclusions

Eight doubly bridged anthracenes with different bridge lengths and functional groups were synthesized and compared to their phenylated, TIPS-ethynylated or literature-known, ether-bridged counterpart(s) with respect to their optoelectronic properties and lightfastness in solution.

The connectivity of the bridge impacts stability - electronwithdrawing ester-based linkers are superior to ether bridges. The lengths of the ester-based bridges only play a minor role, but it is of vital importance to substitute the 9,10-positions of the underlying anthracene. Our ester-bridged derivatives are prepared in reasonable yields via a fourfold esterification synthesis simplified compared to the most photo-stable anthracene 4. Our anthracenes work as OLED emitters: 9, 10 and 12 result in deep blue fluorescent (proof-of-principle) OLEDs, whereas ether-based 3 exhibits a whitish color attributed to excimer emission. Our results highlight that double bridging combines improved lightfastness with deep-blue electroluminescence, which is why these and similar anthracenes are attractive targets as stable emitters for blue OLEDs, provided that the correct functional group for macrocyclization is chosen and that OLED quantum yields can be further improved.

### Supporting Information

The authors have cited additional references within the Supporting Information.  $^{\scriptscriptstyle [50-58]}$ 



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## Conflict of Interests

The authors declare no conflict of interest.

## Data Availability Statement

The data that support the findings of this study are openly available in heiDATA at https://doi.org/10.11588/data/1MXYDJ.

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# **RESEARCH ARTICLE**



A series of bridged anthracenes was synthesized and their photostabilities were accessed. While the length of the bridges only plays a minor role, introduction of electron withdrawing ester-based linkers retards photooxidation most. Those esters bridged anthracenes could be prepared in reasonable yields and "proof-of-principle" organic light emitting diodes with deep blue emission were built, demonstrating their potential as emitters. P. Ludwig, J. Mayer, Dr. L. Ahrens, Dr. F. Rominger, Dr. G. Ligorio, Dr. F. Hermerschmidt, Prof. E. J. W. List-Kratochvil\*, Dr. J. Freudenberg\*, Prof. U. H. F. Bunz\*

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Doubly Bridged Anthracenes: Blue Emitters for OLEDs