Phenylquinoxaline Polymers and Low Molar Mass Glasses as Electron-Transport Materials in Organic Light-Emitting Diodes

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ABSTRACT: We present a new synthetic approach to both phenylquinoxaline polymers and low molar mass glasses. A palladium-catalyzed coupling of arylalkynes and bromobenzenes and subsequent oxidation of the triple bonds lead to the corresponding benziles. Reaction with diaminobenzidine yields poly(phenylquinoxalines) (PPQs), whereas the reaction with 1,2-diaminobenzenes leads to low molar mass bis(phenylquinoxalines) (BPQs) and tris(phenylquinoxalines) (TPQs). Both PPQs and TPQs carry *tert*-butyl or CF_3- substituents and are fully soluble in chlorinated hydrocarbons. The starburst TPQs are able to form stable, low molar mass glasses. Cyclic voltammetry reveals that the TPQs have low-lying lowest unoccupied molecular orbitals levels at about −3.6 eV and are attractive as electron-transport materials in organic light-emitting diodes (LEDs). Two-layer LEDs with poly(phenylenevinylene) were fabricated that show a maximum brightness of 450 cd/m^2.

1. Introduction

Poly(phenylquinoxalines) (PPQs) are known already since 1967 when their synthesis was first described by Hergenrother.[1] They are heat-resistant heterocyclic polymers and have been used as adhesives in the aircraft and space industry in the 80s.

Very recently, PPQs have attracted interest as electron-transport materials in organic light-emitting diodes (OLEDs).

Since the first report on OLEDs in 1987,[2] rapid progress has been made in this field. Bright, energy-efficient OLEDs with lifetimes up to 10.000 h have recently been reported.[3] Many state-of-the-art OLEDs consist of several layers, each of which plays its special role (e.g., it is responsible for the transport of holes or electrons or acts as an emissive layer). Such multilayer LEDs are manufactured by subsequent vacuum evaporation of organic materials on top of an indium tin oxide (ITO) covered glass. A large number of materials have yet been tested in OLEDs. The most popular ones are aromatic amines such as *N*,*N*,*N*′,*N*′-tetrakis(3-methylphenyl)benzidine (TPD) as the hole-transport layer and aluminum trishydroxyquinoline (Alq$_3$) or electron-deficient heterocycles such as oxadiazoles as the electron-transport layer. The materials mentioned above usually form amorphous layers after vacuum evaporation but have a strong tendency to recrystallize due to their low glass-transition temperatures (T_g).

The development of effective strategies to overcome problems related with the morphological instability of evaporated layers is a challenge for synthetic organic chemistry. One promising approach is star-shaped molecules which are able to form stable, low molar mass glasses. Starburst molecules have a well-defined molecular weight, no molecular-weight distribution, no end groups and they can be purified by the standard methods of organic chemistry. Within the last few years, a number of star-shaped hole-transport materials have been synthesized[4] and successfully tested in OLEDs.[5] Nevertheless, only a few star-shaped electron-transport materials have yet been reported.[6−8]

The second class of materials frequently used in OLEDs are polymers. Since the discovery of electroluminescence in poly(1,4-phenylenevinylene) (PPV) in 1990,[9] a large number of polymers have been prepared and tested in organic LEDs. Like with low molar mass materials, most of the polymers are hole-transporting. Prominent examples are PPV and its substituted derivatives.[10]

Several electron-transporting polymers have been reported in the last few years, too. They usually contain electron-deficient heterocycles such as oxadiazoles and triazines as part of the polymer main chain or as side the group.[10−12] In contrast to the large number of papers on oxadiazole polymers, only a few reports on the use of phenylquinoxaline containing polymers in OLEDs exist.[13,14]

In this paper we report a new synthetic approach to both phenylquinoxaline polymers (PPQs) and low molar mass phenylquinoxaline glasses. The synthesis as well as the thermal and optical properties of the novel materials and their use in two-layer LEDs will be discussed in the following chapters.

2. Polyphenylquinoxalines PPQs

Poly(phenylquinoxalines) (PPQs) belong to the class of high-performance thermoplastics that exhibit a high thermal stability and good chemical resistance.

The established synthetic route to polyphenylquinoxalines **5** involves the polycondensation of bis(phenylglyoxaloyl)benzenes (bisbenziles) **3** with 3,3′-diaminobenzidine **4a** in *m*-cresol as the solvent. The bis(phenylglyoxaloyl)benzenes **3** are usually prepared by selenium dioxide oxidation of bis(phenylketo)xylylenes **2** which are obtained by Friedel Crafts acylation[15] (Scheme 1).

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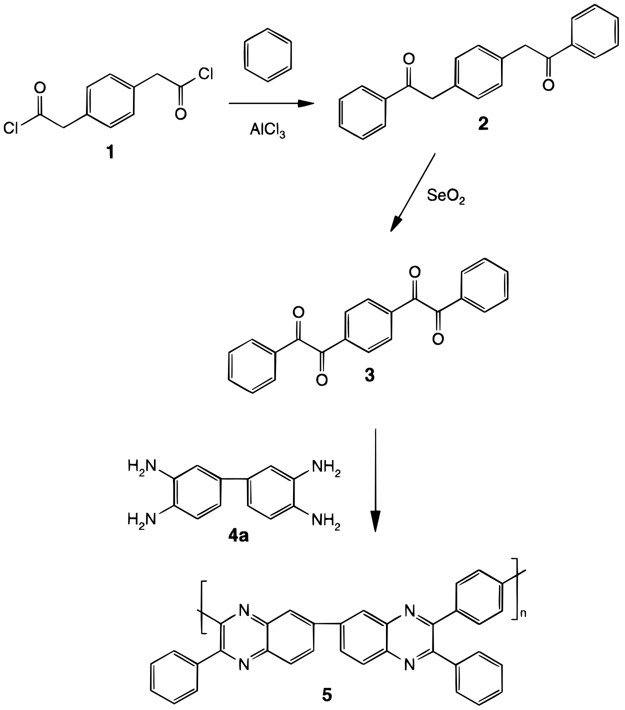
Scheme 1. Common Synthetic Route to Poly(phenylquinoxalines) 5[15]

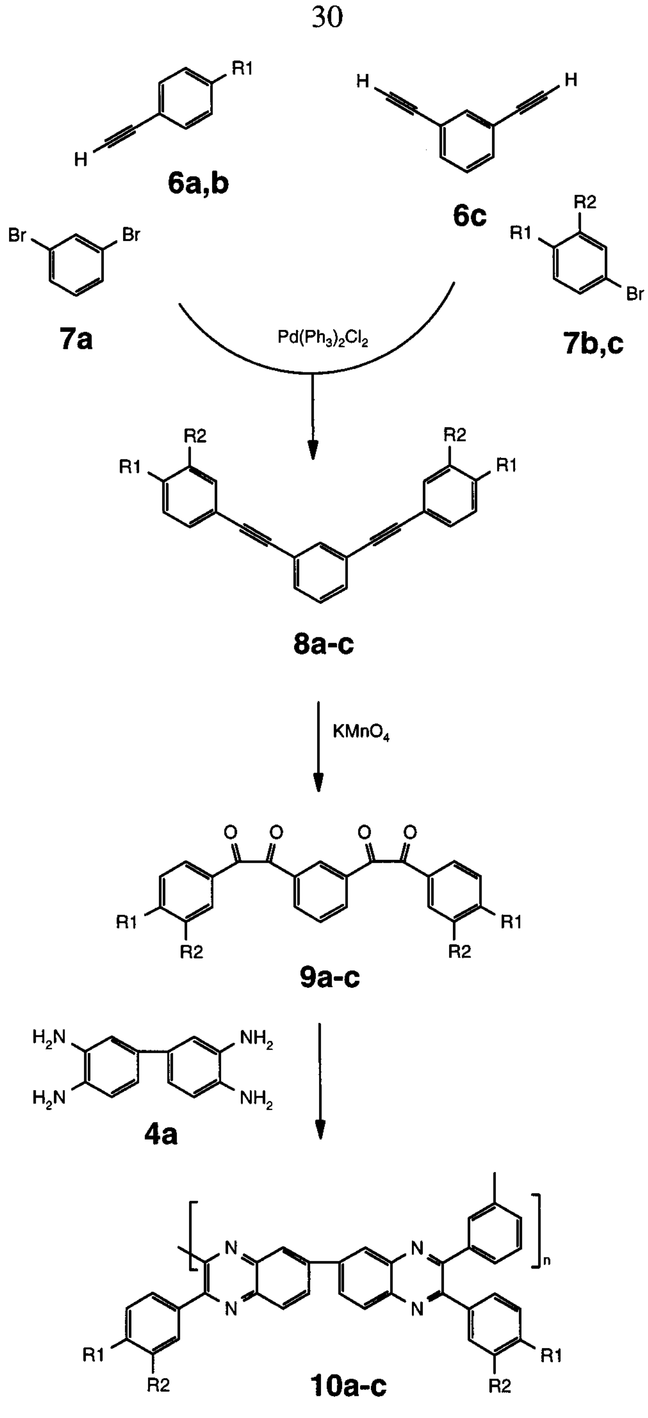


We used a different synthetic approach which is outlined in Scheme 2. The phenylacetylenes **6a,b** and 1,3-dibromobenzene **7a** or alternatively 1,3-diethynylbenzene **6c** and the substituted bromobenzenes **7b,c** were cross-coupled in a palladium-catalyzed Heck reaction[16] to the 1,3-bis(arylalkynes) **8a**−**c**. The 1,3-bis(arylalkynes) **8a**−**c** could easily be oxidized to the tetraketones **9a**−**c** with $KMnO_4$ in acetone according to the procedure for the oxidation of diphenylacetylene described by Srinivasan.[17] The molar ratio of the $KMnO_4$/alkyne group, however, had to be changed to 2:1. This route to the tetraketones **9a**−**c** avoids the use of highly toxic selenium dioxide as the oxidizing agent.

The last step is the polycondensation of the bisbenziles **9a**−**c** and 3,3′-diaminobenzidine **4a** leading to the new substituted PPQs [poly(*m*-phenylene-3,3′-bis(2,2′-diphenyl)quinoxaline-6,6′-diyls)] **10a**−**c**. The polycondensation is usually carried out in *m*-cresol or in mixtures of *m*-cresol and xylene. *m*-Cresol is known to catalyze the polycondensation. However, the use of the high boiling and polar *m*-cresol has several disadvantages. One is the poor removability of the solvent from bulk material or cast fims for LED applications. Since our bisbenziles are substituted with solubilizing *tert*-butyl- or trifluoromethyl groups, the polycondensation can be carried out in pure chloroform in which all three PPQs are soluble.

The molecular weights of the PPQs **10a**−**c** were determined by gel permeation chromatography and are listed in Table 1. The M_w values are in the range from 10 000 up to 15 000 g/mol and M_n is between 3000 and 6000. This corresponds to a degree of polymerization between 20 and 30. One reason for the relatively low molecular weight of the polymers is the limited solubility of the tetramine in chloroform. At the beginning, the tetramine is insoluble but does dissolve throughout the reaction and finally a clear solution is obtained. Nevertheless, the reaction is slowed and this may lead to undesired side reactions of the diketone end groups.

Scheme 2. Synthesis of the PPQs 10a−**c**



PPQ	R1	R2
10a	H	H
10b	*tert.*-Bu	H
10c	H	CF_3

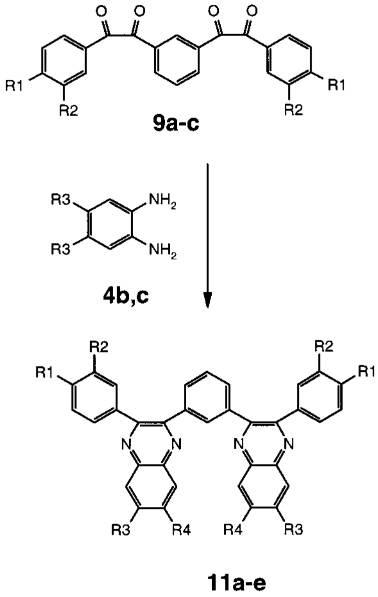
All polymers have good film-forming properties. The glass-transition temperatures are at about 330 °C and thermal decomposition starts at 490 °C (Table 1). The polymers **10a**−**c** exhibit absorption maxima at about 270 and 370 nm in solution. In the solid state the absorption is slightly red-shifted. A weak blue fluorescence with a maximum at about 420 nm is observed in chloroform solution for all three polymers. In the bulk, the fluorescence is red-shifted by about 50 nm.

Table 1. Molecular Weights, Thermal Properties, and Optical Properties of the PPQs

PPQ	M_n[a] [g/mol]	M_w[a] [g/mol]	T_g[b] [°C]	T_{dec}[c] [°C]	PL[d] [nm] sol	PL[d] [nm] film
10a	5500	15 300	329	493	421	471
10b	3600	12 100	326	491	425	461
10c	3400	10 700	329	502	420	493

[a] Determined by GPC in chloroform solution using polystyrene standards. [b] Glass-transition temperature determined by DSC, 20 °C/min, 2nd heating. [c] Thermogravimetric analysis, N_2, onset of decomposition, heating rate 10 K/min. [d] Photoluminescence (PL) maxima in solution (chloroform, $c \approx 10^{-4}$ mol/L) and films on quartz substrates; the excitation wavelength corresponds to the absorption maximum.

Scheme 3. Synthesis of 1,3-bis(3-phenylquinoxaline-2-yls) (BPQs) 11a−e



BPQ	R1	R2	R3	R4
11a	H	H	CH_3	CH_3
11b	H	H	CF_3/H	
11c	*tert.*-Bu	H	CH_3	CH_3
11d	*tert.*-Bu	H	CF_3/H	
11e	H	CF_3	CH_3	CH_3

3. Bis(Phenylquinoxalines) BPQs (Model Compounds)

Another approach to OLED materials are low molar mass glasses. From these compounds thin layers can be manufactured by either solution processing or vacuum deposition. LED devices demand fully amorphous materials (e.g., glasses) that do not crystallize under the operation conditions and that form homogeneous thin films.

With this in mind we synthesized low molar mass compounds on the basis of phenylquinoxalines. Both solubility and glass-forming properties are implemented by the attachment of bulky *tert*-butyl or trifluoromethyl groups.

According to Scheme 3 the bis(phenylquinoxalines) (BPQs) **11a**−**e** have been synthesized by the condensation of the tetraketones **9a**−**c** with the substituted phenylenediamines **4b**,**c**. Subsequent purification involved chromatography and sublimation. Chemical structure and molecular uniformity have been checked by FT-IR, ^{1}H NMR, and ^{13}C-NMR, mass spectrometry, and GPC analysis (refer to the Experimental Section).

The BPQs **11b**,**d** are prepared by the reaction of the corresponding tetraketones **9a**,**b** with 4-trifluoromethyl-1,2-phenylendiamine **4c**. In this reaction three isomers are formed (Scheme 4). We were able to isolate one isomer by column chromatography to which we assign structure A (refer to Experimental Section). As it will be discussed in detail in section 5, the formation of isomeric mixtures strongly favors the formation of glassy materials.

The thermal, optical, and electrochemical properties are given in Table 2. Two absorptions at 255 and about 355 nm are observed in the UV/Vis spectra which can be assigned to the phenyl and quinoxaline moieties, respectively. All bis(phenylquinoxalines) BPQs show pale blue fluorescence in the solid state, which is only slightly red-shifted in comparison to the fluorescence in solution. The optical data will be discussed in section 5.

4. Tris(phenylquinoxalines) (TPQs)

We have used the novel route, that we have worked out for the synthesis of poly(phenylquinoxalines) for the preparation of starburst 1,3,5-tris(phenylquinoxalines).

The synthetic pathway to the TPQs **15a**−**h** (Scheme 5) starts with the palladium-catalyzed cross coupling of the phenylacetylenes **6a**,**b** with 1,3,5-tribromobenzene **12a** to the tris(phenylethinyl)benzenes **13a**−**c** which are obtained in about 70% yield.[16] In this reaction 1,4-diphenyldiacetylene is always formed as a byproduct, but it can be easily removed by recrystallization of the TPQs from 2-propanol. Unlike the 1,3-bis(arylalkynes) **8a**−**c** the trifunctional alkynes **13a**−**c** cannot be oxidized with $KMnO_4$ in acetone. Several attempts yielded no hexaketone but only over-oxidized compounds with carboxylic groups. Instead, the 1,3,5-tris(phenylglyoxaloyl)benzenes **14a**−**c** were prepared via NBS oxidation in anhydrous dimethyl sulfoxide.[18] Subsequent condensation with the substituted 1,2-phenylendiamines **4b**−**d** led to the 1,3,5-tris(3-phenylquinoxaline-2-yl)benzenes (TPQs) **15a**−**f**. The 1,3,5-tris(3-phenylquinoxaline-2-yl-phenyl)benzenes **15g**,**h** with a triphenylbenzene core were prepared by an analogous procedure starting from 1,3,5-tris(4-bromophenyl)benzene.[19] All compounds were characterized by IR and NMR spectroscopy and mass spectroscopy (for details see Experimental Section).

5. Thermal Properties

The thermal properties of the TPQs **15a**−**h** were determined by DSC and TG measurements.

As illustrated in Figure 1 the glass-transition temperatures of the bis(phenylquinoxalines) BPQs **11a**−**e** range from 95 °C up to 139 °C. Attachment of one more 3-phenylquinoxaline-2-yl side arm raises the values to 147−195 °C for the TPQs. The glass-transition temperatures of the TPQs are closely related to the substitution pattern (Figure 1). The introduction of *tert*-butyl groups (filled signs) leads to a small increase of the T_g's compared to those of the unsubstituted ones (open signs). Dimethyl substitution of the quinoxaline moieties (circles) induces higher T_g's than CF_3 substitution (triangles) does. Though for some TPQs (**15b**,**d**,**e**) a melting point could be detected in the first DSC run, upon cooling and in a second and third heating cycle no recrystallization is observed in all TPQs. Even annealing experiments of **15b**−**e** (5 h at 250 °C) did not induce recrystallization. X-ray measurements of a 150-

Scheme 4. Constitutional Isomers of BPQ 11d

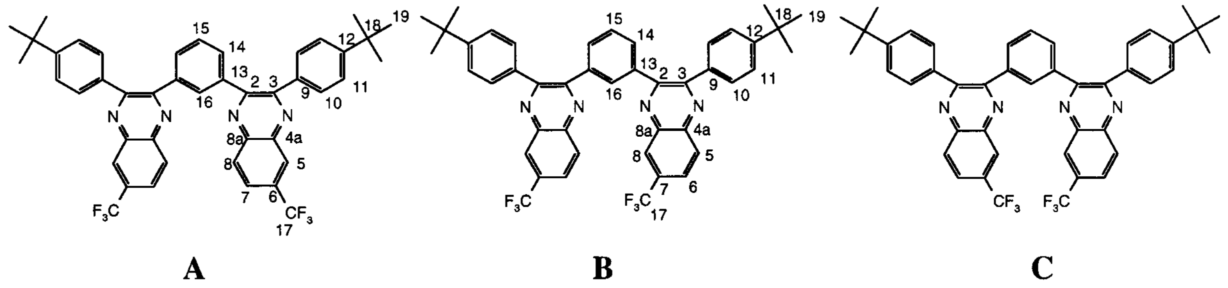


Table 2. Molecular Weights, Thermal Properties, and Optical Properties of the BPQs

BPQ	M_w	T_g[a] [°C]	T_m[b] [°C]	T_{dec}[c] [°C]	PL[d] sol	PL[d] film
11a	542	119	237	385	397	405
11b	622	95		306	410	416
11c	654	139	286	404	402	417
11d	724	106	205	294	419	425
11e	678	115		334	401	401

[a] Glass-transition temperature determined by DSC, 20 °C/min, 2nd heating. [b] Melting point measured by DSC, 20 °C/min. [c] Thermogravimetric analysis, N_2, onset of decomposition, heating rate 10 K/min. [d] Photoluminescence (PL) maxima in solution (chloroform, $c \approx 10^{-4}$ mol/L) and films on quartz substrates; the excitation wavelength corresponds to the absorption maximum.

nm thick film of evaporated **15c** (evaporation rate = 4 Å/min) shows that the film is fully amorphous.

The stability of the glassy state can be fine-tuned by varying the substitution pattern. The most stable glasses are obtained with trifluoromethyl or *tert*-butyl groups. In the trifluoromethyl-substituted BPQs and TPQs the synthesis leads to three isomers for the BPQs **11b**,**d** and four isomers for the TPQs **15c**,**f**,**g** which further decrease the ability to crystallize. The same trend is observed in the TPQs **15g**,**h** in which the rigid benzene core is replaced by the more flexible triphenylbenzene.

6. Optical Characterization of TPQs

The optical and the fluorescence properties of a material strongly affect its performance in an OLED.

Interesting phenomena are observed concerning the fluorescence of the TPQs **15a**−**c** without tert-butyl groups attached to the phenyl ring. In solution pale blue fluorescence in the 400-nm range is observed, whereas in the film spectra a new peak appears at about 500 nm, exceeding the former in intensity. We attribute the greenish fluorescence to the ability of the TPQs **15a**−**c** to form complexes that lead to excimer fluorescence (Figure 2).

TPQs **15d**−**f** show pale blue fluorescence both in solution and in the solid state. The maximum of the fluorescence in the film is only slightly red-shifted compared to that of the solution. We explain this by the assumption that sterically demanding groups such as *tert*-butyl prevent “disc-like” molecules from stacking on top of each other, and consequently excimer fluorescence is suppressed.

In the case of the TPQs **15a**−**c** the tendency for molecules to associate is enlarged by increasing the concentration (refer to Figure 3). Figure 3 shows that the greenish excimer fluorescence at 500 nm becomes stronger with an increasing concentration of **15c** in chloroform. Similar association phenomena have been observed in NMR studies of oxadiazole dendrimers.[6]

As shown in Figure 2 excimer fluorescence is present in TPQs with −H, $-CH_3$, and CF_3 substituents and is absent in the compounds **15d**−**f** with *tert*-butyl groups. In the solid state the situation for **15f** is slightly different. The fluorescence spectrum of a freshly prepared film of **15f** with both $-CF_3$ and *tert*-butyl groups shows virtually no excimer fluorescence (Figure 4). After 6 weeks of storage a shoulder appears at 500 nm which is the wavelength of the excimer emission. This indicates that molecular reorientation in the glassy state is possible even at temperatures 140 °C below the glass-transition temperature in these materials.

7. Cyclic Voltammetry

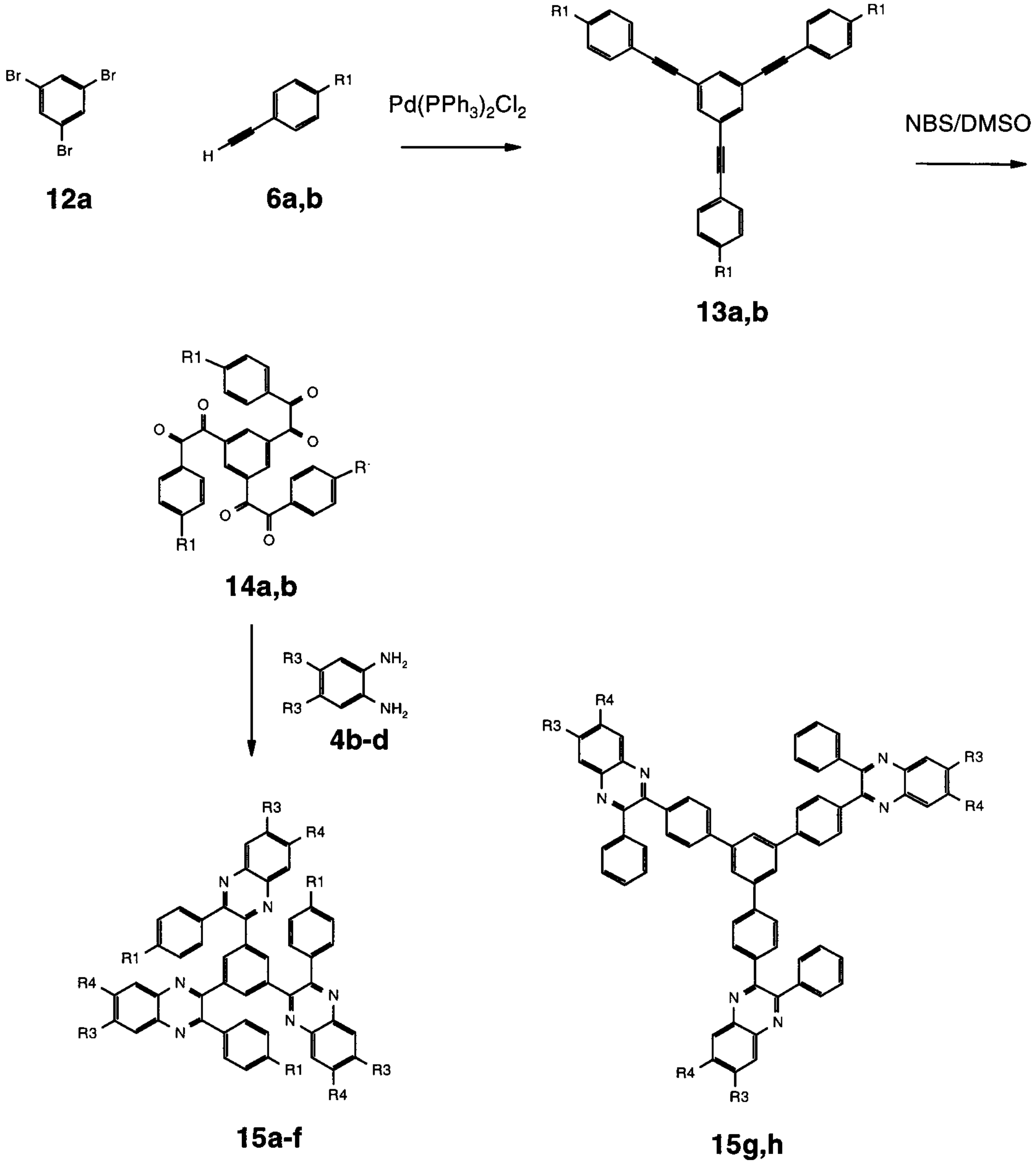
Trifluoromethyl-substituted BPQs and TPQs are soluble in acetonitrile and were investigated by cyclic voltammetry. The TPQs **15c**,**f** exhibit a reduction potential of −1.78 V (vs fc/fc$^+$). Regarding the energy level of the ferrocen/ferrocenium reference, one can calculate the lowest unoccupied molecular orbital (LUMO) energies with the assumption that the LUMO level of ferrocen/ferrocenium is 4.8 eV below vacuum.[20] Since the ferrocen/ferrocenium−LUMO level is determined by photoelectron spectroscopy in the solid state, this method can only be considered to be a rough approximation. In solution a LUMO level is obtained by cyclic voltammetry for commercial PBD at −2.4 eV.[20] Investigations by means of photoelectron spectroscopy [21] show that this value is lowered to −3.0 eV in the solid state. Our own measurements for oxadiazole derivatives also reveal a shift of around −0.5 eV from solution to the solid state.[22] So we assume that the LUMO energy level of the TPQs **15c**,**f** will be at about −3.6 eV. Regarding the optical band gap derived from the absorption spectra, we can calculate highest occupied molecular orbital (HOMO) levels between 6.6 and 6.8 eV (Table 4).

Figure 5 shows the energy level diagram of a two-layer LED with PPV as the hole-transport layer and the TPQ **15c**. The HOMO and LUMO levels for ITO[23] and PPV[24] were taken from literature. The energetic position of the LUMO at −3.6 eV suggests that in the case of the TPQs a significantly enhanced electron injection into the ETL layer is to be expected as compared with commercial 2-(4-biphenylyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (PBD). The energy barrier for holes between the PPV/TPQ interface is larger than that for electrons, so that the TPQs act as an effective hole-blocking layer.

8. Fabrication and Characterization of Two-Layer Devices

Due to their excellent film-forming properties, homogeneous transparent films could be spin cast from

Scheme 5. Synthesis of 1,3,5-tris(3-phenylquinoxaline-2-yl)benzenes (TPQs) 15a–h



TPQ	Core	R1	R3	R4
15a	C_6H_3	H	H	H
15b	C_6H_3	H	CH_3	CH_3
15c	C_6H_3	H	CF_3/H	
15d	C_6H_3	*tert.*-Bu	H	H
15e	C_6H_3	*tert.*-Bu	CH_3	CH_3
15f	C_6H_3	*tert.*-Bu	CF_3/H	
15g	$(C_6H_4)_3C_6H_3$	H	CF_3/H	
15h	$(C_6H_4)_3C_6H_3$	H	CH_3	CH_3

BPQs, TPQs, and PPQs, which were applied in two-layer LEDs together with PPV as the hole-transport layer (configuration: ITO/PPV (150 nm)/quinoxaline (30 nm)/Ag). In all cases the electroluminescence (EL) spectra of the multilayer LEDs are identical to those of single-layer PPV devices (i.e., the LEDs emit yellowish-green light. This is in agreement with the lower barrier between the LUMOs of PPV and TPQ compared to the corresponding HOMO levels, so that recombination takes place in the PPV layer close to the PPV/TPQ interface.

Our single-layer EL devices from PPV usually show low luminescence efficiencies (about 0.001% external quantum efficiency in the configuration ITO/PPV/Al). This is obviously due to the fact that these devices are majority carrier devices (Schottky diodes), and there is a large excess hole current leading to an unbalanced current flow.

Our measurements of two-layer LEDs with the configuration ITO/PPV(150 nm)/phenylquinoxaline (30 nm)/Ag confirm that all tested phenylquinoxalines act as efficient electron-injection and -transport layers and are hole-blocking. The devices show a considerable increase in the physiological brightness (2 orders of magnitude) and quantum efficiency compared to PPV single-layer devices (Figure 7).

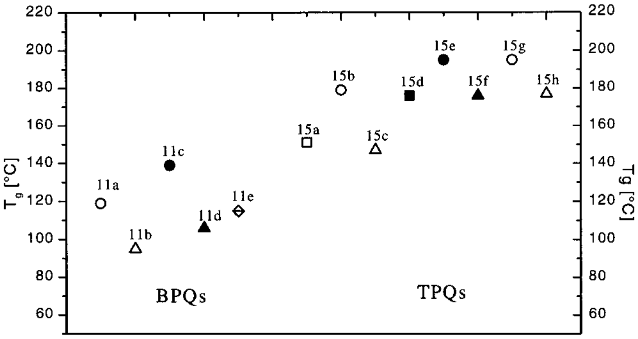


Figure 1. Glass-transition temperatures of BPQs and TPQs.

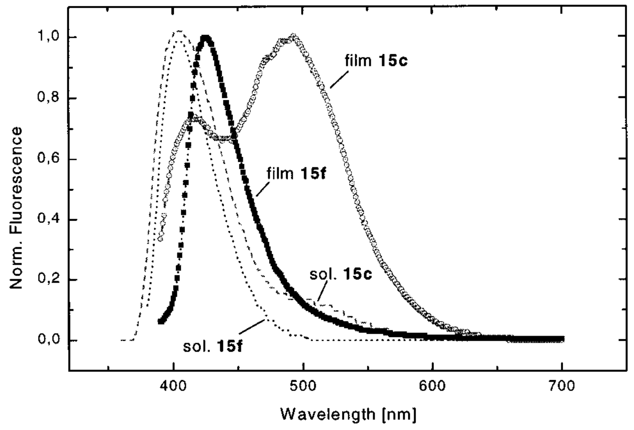


Figure 2. Normalized fluorescence spectra of the TPQs **15c** and **15f** in chloroform solution and from films on quartz substrates.

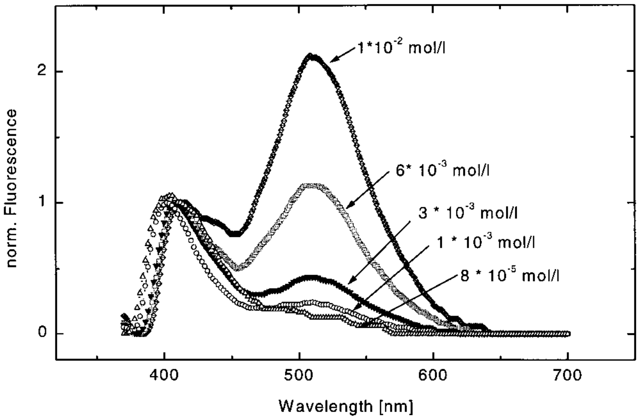


Figure 3. Concentration-dependent fluorescence spectra of the TPQ **15c** in chloroform solution (spectra normalized to an intensity of 1 at 400 nm).

The threshold voltage for electroluminescence ranges from 5.7 V for the TPQ **15c** to 10 V for **15a** (Figure 6). The threshold voltages for the polymers **10a**−**c** are between 8 and 10 V (Figure 8). The maximum luminance for TPQ devices is about 200 cd/m^2 (η_{ext} = 0.11%) for TPQs and 400−450 cd/m^2 (η_{ext} = 0.13%) for PPQ polymers, respectively (Table 5).

The hole-blocking properties of the TPQs result from the high barrier between the HOMO levels of PPV and TPQ (1.7 eV; Figure 5). This together with the position of the corresponding LUMOs (barrier 1.0 eV) supports the assumption that carrier transport is limited by space charges. Only a few holes (electrons) can be transported into the TPQ (PPV) layer which leads to an accumulation of charge carriers close to the PPV/TPQ interface.

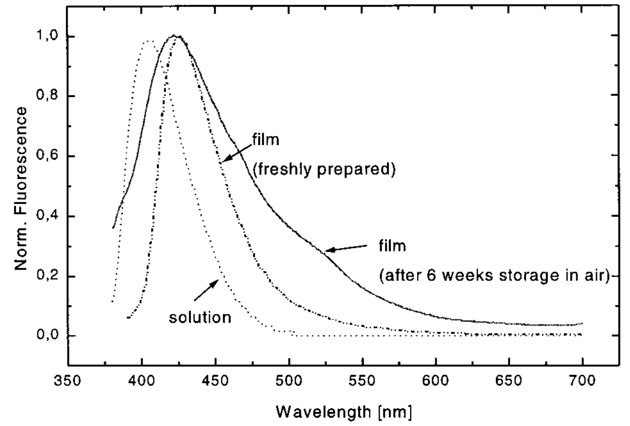


Figure 4. Fluorescence spectra of **15f** in solution and as film.

Table 3. Molecular Weights, Thermal Properties, and Optical Properties of the TPQs

TPQ	M_w	T_g[a] [°C]	T_m[b] [°C]	T_{dec}[c] [°C]	PL[d] [nm] sol	PL[d] [nm] film
15a	690	151		414	395	415/515
15b	774	179	361	408	402	412/516
15c	894	147		370	403	417/493
15d	858	176	351	401	401	414
15e	942	195	391	406	399	410
15f	1062	165		363	406	426
15g	1122	177		453	426	425
15h	1002	195		484	406	419/529

[a] Glass-transition temperature determined by DSC, 20 °C/min, 2nd heating. [b] Melting point measured by DSC, 20 °C/min. [c] Thermogravimetric analysis, N_2, onset of decomposition, heating rate 10 K/min. [d] Photoluminescence (PL) maxima in solution (chloroform, $c \approx 10^{-4}$ mol/L) and films on quartz substrates; the excitation wavelength corresponds to the absorption maximum.

Table 4. Energetic Level Data for Some BPQs and TPQs

BPQ/TPQ	$E_{red\,[V]}$[a] (vs fc/fc$^+$)	LUMO[b] [eV]	LUMO[c] [eV]	band gap[d] [eV]	HOMO [eV]
11d	−1.79	−3.0	−3.6	3.1	−6.8
11e	−2.03	−2.8	−3.4	3.2	−6.6
15c	−1.78	−3.0	−3.6	3.2	−6.8
15f	−1.78	−3.0	−3.6	3.2	−6.8

[a] Measured in acetonitrile solution containing 0.1 mol/L of $[(H_9C_4)N]PF_6$. [b] Calculated with the assumption that the energy level of ferrocen/ferrocenium is 4.8 eV below vacuum[22]. [c] Adapted to solid-state values (refer to text). [d] Optical band gap derived from film absorption spectra.

The accumulation induces the formation of space charges that make further charge-carrier transport more difficult. As a consequence, increasing the voltage only leads to an increase of the electric field at the interface but to a decrease of the slope of the luminance curves which is in agreement with Figures 6 and 8. With respect to this we suppose that these results do not represent the whole potential of the phenylquinoxalines.

Further optimization will be carried out with different device configurations and hole-transport layer (HTL) materials.

9. Conclusion

We have presented a novel synthetic route to phenylquinoxaline polymers (PPQs) and low molar mass glasses, bis(phenylquinoxalines) (BPQs) and tris(phenylquinoxalines) (TPQs).

The palladium-catalyzed coupling of arylalkynes and bromobenzenes and subsequent oxidation of the triple bonds leads to the corresponding benziles. Reaction

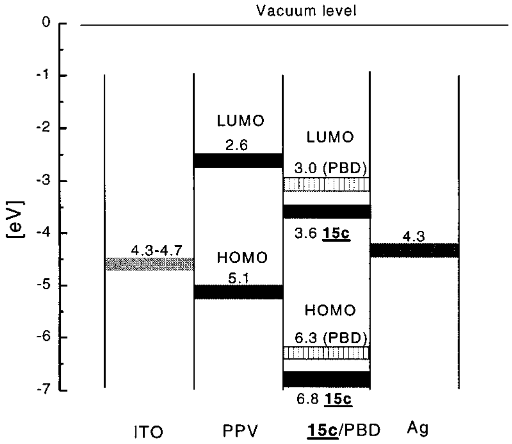


Figure 5. Energy level diagram of PPV/TPQ two-layer diodes (for details refer to text).

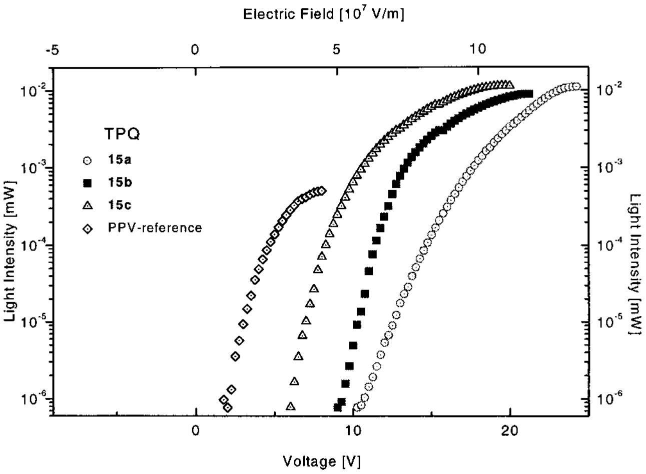


Figure 6. Plot of light intensities vs bias (electric field) for LEDs with configuration ITO/PPV(150 nm)/TPQ(30 nm)/Ag.

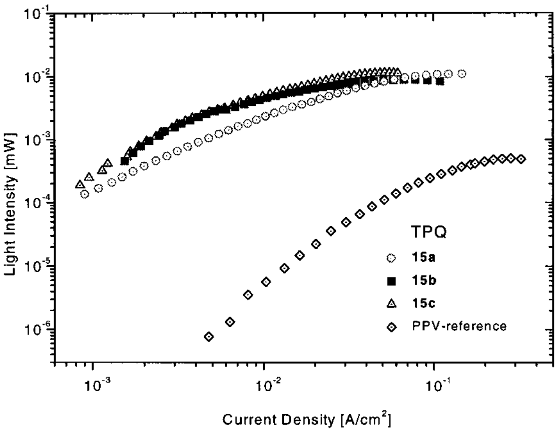


Figure 7. Plot of light intensities vs current density for ITO/PPV(150 nm)/TPQ(30 nm)/Ag OLEDs.

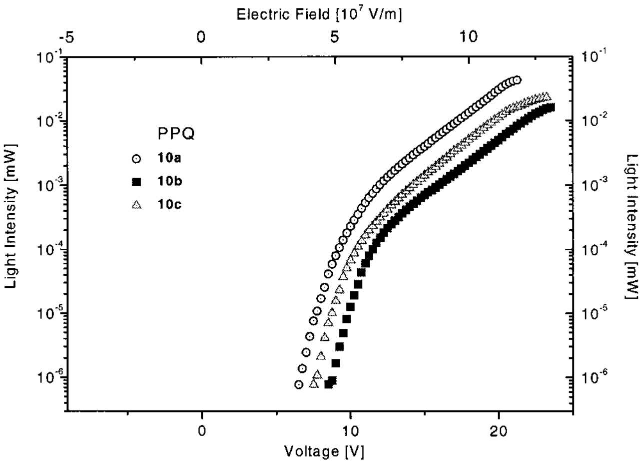


Figure 8. Plot of light intensities vs bias (electric field) for LEDs with configuration ITO/PPV(150 nm)/PPQ(30 nm)/Ag.

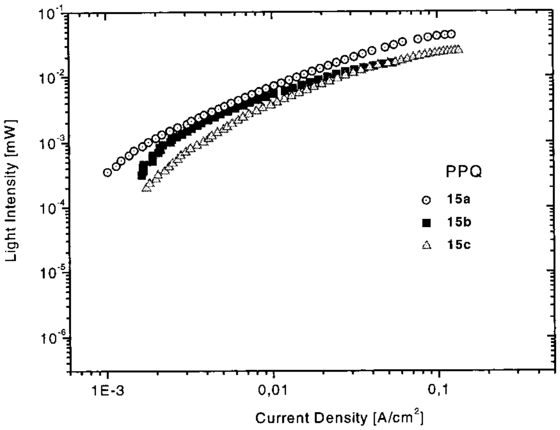


Figure 9. Plot of light intensities vs current density for ITO/PPV(150 nm)/PPQ(30 nm)/Ag OLEDs.

Table 5. Onset Voltages, Light Intensities, and External Quantum Efficiencies of ITO/PPV (150 nm)/Quinoxaline (30 nm)/Ag Devices

quinoxaline	onset voltage [V]	peak luminance [cd/m^2] (at 25 V)	max. ext. quantum yield [%]
10a	6.4	415	0.13
10b	7.4	457	0.11
10c	8.4	360	0.07
11a	6.7	105	0.07
11c	8.4	181[a]	0.05
11d	15.2	205[b]	0.01
15a	10.4	166	0.05
15c	8.4	192[a]	0.10
15d	5.7	236	0.11
PPV reference	2.5	40[c]	0.001

[a] At 20 V. [b] At 43 V. [c] At 13 V.

with diaminobenzidine yields poly(phenylquinoxalines) whereas the reaction with 1,2-diaminobenzenes leads to low molar mass bis(phenylquinoxalines) and tris(phenylquinoxalines). This synthetic pathway avoids the use of highly toxic SeO_2 as the oxidizing agent which is applied in the traditional synthesis.

Both PPQ polymers and TPQs carry *tert*-butyl and CF_3 substituents and are fully soluble in chlorinated hydrocarbons. The starburst tris(phenylquinoxalines) TPQs form low molar mass glasses. Their substitution pattern has a strong influence on the stability of the glassy state. It is shown that TPQs with *tert*-butyl substituents or isomeric mixtures of CF_3-substituted TPQs form the most stable glasses.

Fluorescence measurements show that TPQs without bulky substituents exhibit excimer fluorescence which is suppressed in highly substituted TPQs. Cyclic voltammetry reveals that the CF_3-substituted TPQs have a low-lying LUMO level at about −3.6 eV. The phenylquinoxalines have been tested in two-layer LEDs with PPV. Both brightness and quantum efficiency are significantly increased compared to our monolayer devices. The novel PPQs and TPQs will be tested in other LED architectures soon.

10. Experimental Section

Device Fabrication and LED measurement. For device fabrication a thin layer of a PPV precursor was cast from solution onto a pattered indium tin oxide (ITO) coated glass substrate. This film was converted to PPV by annealing at 160 °C in an argon atmosphere for 2 h. PPQ, BPQ, or TPQ films were spin-coated from chloroform solution (0.25 wt %) on top of the PPV layer to give a transparent film. A silver electrode was vacuum-deposited at pressures below 10^{-6} mbar.

LEDs were prepared with a PPV-layer thickness of 150 nm and with phenylquinoxaline films of 30 nm on top. The active area of the devices was 25 mm^2. To enable a direct comparison of the experimental data, the devices were prepared under identical conditions and a PPV monolayer LED was made for comparison. All measurements were carried out under ambient conditions.

The current−voltage (I−V) characteristics and light intensities were simultaneously measured with a Keithley 237 source measure unit and a Bentham silicon photodiode (DH−Si) in a calibrated Ulbricht sphere. The brightness was determined with a Minolta Chroma Meter CS-100.

Synthetic Procedures. 1,3-Bis(phenylethynyl)benzene (8a) was prepared according to **8b**. Yield: 4.2 g (70%) of colorless needles; T_m =112 °C. IR (KBr): 1595, 1570, 1490, 1410, 1070, 903, 802 cm^{-1}. ^{1}H NMR (CDCl$_3$): 6.85 ($\mathrm{C_{Ar}}$**H**, t, 1H), 7.33 ($\mathrm{C_{Ar}}$**H**, t, 4H), 7.37 ($\mathrm{C_{Ar}}$**H**, t, 2H), 7.45 ($\mathrm{C_{Ar}}$**H**, dd, 2H), 7.50 ($\mathrm{C_{Ar}}$**H**, dd, 4H), 7.7 ($\mathrm{C_{Ar}}$**H**, t, 1H) ppm. ^{13}C NMR (CDCl$_3$): 88.5 ($\mathrm{C}_{\mathbf{alkyne}}$), 90.0 ($\mathrm{C}_{\mathbf{alkyne}}$), 122.9, 123.6, 128.3, 128.6, 131.2, 131.6, 134.5 ppm.

1,3-Bis(4-*tert*-butylphenylethynyl)benzene (8b). All other phenylethynylbenzenes were prepared according to the following procedure. First, 2.66 mL (22 mmol) of 1,3-dibromobenzene is dissolved in 70 mL of anhydrous NEt$_3$ and 30 mL of pyridine in a dry flask under argon. The solution is treated by two freeze−thaw cycles to remove traces of oxygen, before 0.3 g of Pd(PPh$_3$)$_2$Cl$_2$ [0.43 mmol], 0.6 g of PPh$_3$ [2.29 mmol], and 0.1 g of CuI [0.52 mmol] are added and an additional freeze−thaw cycle is carried out. To activate the catalyst, the mixture is stirred and heated to 70 °C. In a second flask, 9 mL [50.6 mmol] of 4-*tert*-butylphenylacetylene are dissolved in 10 mL of pyridine, treated according to the procedure above, and transferred into a dropping funnel. Subsequently, the phenylacetylene is added over a period of about 5 h. After being stirred for 24 h at 70 °C, the reaction mixture is poured into an excess of diluted HCl. The precipitate is filtered off and dissolved in CH$_2$Cl$_2$. The solution is washed with diluted HCl and water and was allowed to evaporate. The crude product is purified by recrystallization from 2-propanol. Yield: 5.7 g (66%) of colorless needles; T_m = 135 °C. IR (KBr): 1588, 1567, 1465, 1363, 898, 832, 801 cm^{-1}. ^{1}H NMR (CDCl$_3$): 1.36 (C(C**H**$_3$)$_3$, s, 18H), 7.33 ($\mathrm{C_{Ar}}$**H**, t, 1H), 7.40 ($\mathrm{C_{Ar}}$**H**, **AA′**XX′, 4H), 7.50 ($\mathrm{C_{Ar}}$**H**, dd, 2H), 7.52 ($\mathrm{C_{Ar}}$**H**, AA′**XX′**, 4H), 7.77 ($\mathrm{C_{Ar}}$**H**, t, 1H) ppm. ^{13}C NMR (CDCl$_3$): 31.3 (C(**C**H$_3$)$_3$), 35.0 (**C**(CH$_3$)$_3$), 88.6 ($\mathrm{C}_{\mathbf{alkyne}}$), 90.7 ($\mathrm{C}_{\mathbf{alkyne}}$), 120.8, 124.6, 126.1, 129.2, 131.9, 132.2, 135.4, 152.6 ppm.

1,3-Bis[(3-trifluoromethylphenyl)ethynyl]benzene (8c). Yield: 50% of a colorless solid; T_m = 92 °C. IR (KBr): 3077, 2915, 2215, 1891, 1640, 1489, 1432, 1340, 1167 ($\mathrm{Ar}_{\mathbf{C-F}}$), 903 cm^{-1}. ^{1}H NMR (CDCl$_3$): 7.36 ($\mathrm{C_{Ar}}$**H**, t, 2H), 7.48 ($\mathrm{C_{Ar}}$**H**, t, 2H), 7.52 ($\mathrm{C_{Ar}}$**H**, dd, 2H), 7.60 ($\mathrm{C_{Ar}}$**H**, d, 2H), 7.69 ($\mathrm{C_{Ar}}$**H**, d, 2H), 7.73 ($\mathrm{C_{Ar}}$**H**, s, 1H), 7.80 ($\mathrm{C_{Ar}}$**H**, s, 2H) ppm. ^{13}C NMR (CDCl$_3$): 88.5 ($\mathrm{C}_{\mathbf{alkyne}}$), 89.8 ($\mathrm{C}_{\mathbf{alkyne}}$), 123.1, 123.7 (C−**C**F$_3$, q, $^1J_{C-F}$ = 270 Hz), 123.9, 125.0 ($\mathrm{C_{Ar}}$, q, $^3J_{C-F}$ = 3.8 Hz), 128.4 ($\mathrm{C}_{\mathbf{Ar}}$, q, $^3J_{C-F}$ = 3.8 Hz), 128.7, 128.9, 131.0 ($\mathrm{C}_{\mathbf{Ar}}$**C**−CF$_3$, q, $^2J_{C-F}$ =32 Hz), 131.8, 134.7, 134.8 ppm.

1,3,5-Tris(phenylethynyl)benzene (13a)[16]. Yield: 70% of colorless needles; T_m = 145 °C. IR (KBr): 1597, 1580, 1488, 909, 872, 752, 686 cm^{-1}. ^{1}H NMR (CDCl$_3$): 7.30 ($\mathrm{C_{Ar}}$**H**, m, 3H), 7.30−7.35 ($\mathrm{C_{Ar}}$**H**, m, 6H), 7.50 ($\mathrm{C_{Ar}}$**H**, dd, 6H), 7.63 ($\mathrm{C_{Ar}}$**H**, s, 3H) ppm. ^{13}C NMR(CDCl$_3$): 87.8 ($\mathrm{C}_{\mathbf{alkyne}}$), 90.5 ($\mathrm{C}_{\mathbf{alkyne}}$), 122.7, 123.9, 128.3, 128.5, 131.6, 133.9 ppm.

1,3,5-Tris[(4-*tert*-butylphenyl)ethynyl]benzene (13b). Two recrystallizations from 2-propanol and hexane yield 66% of a white solid. IR (KBr): 2960, 2900, 2210, 1579, 1552, 1463, 1363, 1266, 1103, 1016, 832 cm^{-1}. ^{1}H NMR (CDCl$_3$): 1.40 (C(C**H**$_3$)$_3$, s, 27H), 7.40 ($\mathrm{C_{Ar}}$**H**, **AA′**XX′, 6H), 7.50 ($\mathrm{C_{Ar}}$**H**, AA′**XX′**, 6H), 7.63 ($\mathrm{C_{Ar}}$**H**, s, 3H) ppm. ^{13}C NMR (CDCl$_3$): 31.15, 34.80, 87.34, 90.59, 119.83, 124.16, 125.39, 131.43, 133.80, 151.84 ppm.

1,3,5-Tris[4-(phenylethynyl)phenyl]benzene (13c). Yield: 70% of a white solid; T_m = 208 °C. IR (KBr): 3050, 1594, 1511, 1440, 1390, 1069, 1018, 913, 828, 753 cm^{-1}. ^{1}H NMR (CDCl$_3$): 7.35 ($\mathrm{C_{Ar}}$**H**, m 6H), 7.55 ($\mathrm{C_{Ar}}$**H**, m, 9H), 7.64 ($\mathrm{C_{Ar}}$**H**, **AA′**XX′, 6H), 7.69 ($\mathrm{C_{Ar}}$**H**, AA′**XX′**, 6H), 7.79 ($\mathrm{C_{Ar}}$**H**, s, 3H) ppm. ^{13}C NMR(CDCl$_3$): 89.3 ($\mathrm{C}_{\mathbf{alkyne}}$), 90.4 ($\mathrm{C}_{\mathbf{alkyne}}$), 122.7, 123.2, 125.1, 127.2, 128.3, 128.4, 131.6, 132.1, 140.5, 141.7 ppm.

1,3-Bis(phenylglyoxaloyl)benzene (9a) was prepared by a slight modification of the procedure given in the literature.[17] First, 1 g (3.6 mmol) of 1,3-bis(phenylethynyl)benzene (**8a**) is dissolved in 400 mL of acetone and a buffer solution (0.5 g of NaHCO$_3$ (4.4 mmol) and 2.5 g (10 mmol) of MgSO$_4$·7H$_2$O in 60 mL of water) is added. Two equiv of KMnO$_4$, 2.3 g (14 mmol), are added to the mixture in one portion, followed by stirring for 4 h. Proceeding of the reaction is easily monitored by thin-layer chromatography. After acidification with dilute H$_2$SO$_4$, the oxidation is stopped by adding NaNO$_2$. MnO$_2$ is filtered off, and the yellow product is extracted with hexane/ether 1:1. The hexane/ether mixture is evaporated, and the crude product is redissolved in ether and washed with NaHCO$_3$ and water. Evaporation of the solvent and recrystallization from 2-propanol yields 1.13 g (92%) of yellow crystals; T_m = 100 °C. IR (KBr): 1680, 1663, 1596, 1580, 1450, 1428, 1327, 1225, 1167, 961, 914, 863 cm^{-1}. ^{1}H NMR (CDCl$_3$): 7.54 ($\mathrm{C_{Ar}}$**H**, t, 4H), 7.65 (C**ArH**, t, 1H), 7.65 ($\mathrm{C_{Ar}}$**H**, t, 2H), 7.98 ($\mathrm{C_{Ar}}$**H**, dd, 4H), 8.25 ($\mathrm{C_{Ar}}$**H**, dd, 2H), 8.60 ($\mathrm{C_{Ar}}$**H**, t, 1H) ppm. ^{13}C NMR (CDCl$_3$): 129.1, 129.8, 130.0, 130.7, 132.5, 133.7, 135.2, 135.4, 192.7 ($\mathrm{C_{ketone}}$), 193.3 ($\mathrm{C_{ketone}}$) ppm.

1,3-Bis[(4-*tert*-butylphenyl)glyoxaloyl]benzene (9b) and 1,3-Bis[(3-trifluormethylphenyl)glyoxaloyl]benzene (9c). Reaction proceeded according to **9a**; recrystallization from MeOH. **9b** yield: 83% of a yellow solid; T_m = 121 °C. IR (KBr): 2964, 1672, 1599, 1411, 1229, 1168, 1110, 675, 546 cm^{-1}. ^{1}H NMR (CDCl$_3$): 1.34 (C(C**H**$_3$)$_3$, s, 18H), 7.52 ($\mathrm{C_{Ar}}$**H**, **AA′**XX′, 4H), 7.64 ($\mathrm{C_{Ar}}$**H**, t, 4H), 7.90 ($\mathrm{C_{Ar}}$**H**, AA′**XX′**, 4H), 8.22 ($\mathrm{C_{Ar}}$**H**, dd, 2H), 8.58 ($\mathrm{C_{Ar}}$**H**, t, 1H) ppm. ^{13}C NMR (CDCl$_3$): 30.9 (C−C(**C**H$_3$)$_3$), 35.4 (C−**C**(CH$_3$)$_3$), 126.1, 129.7, 130.0, 130.0, 130.7, 133.9, 137.4, 159.0, 192.9 ($\mathrm{C_{ketone}}$), 193.0 ($\mathrm{C_{ketone}}$) ppm. **9c** yield: 50% of a yellow solid; T_m = 108 °C. IR (KBr): 2924, 1673, 1611, 1596, 1451, 1341, 1289, 1150, 1132, 1069, 959, 924, 800, 695 cm^{-1}. ^{1}H NMR (CDCl$_3$): 7.70 ($\mathrm{C_{Ar}}$**H**, t, 2H), 7.74 ($\mathrm{C_{Ar}}$**H**, t, 1H), 7.95 ($\mathrm{C_{Ar}}$**H**, d, 2H), 8.19 ($\mathrm{C_{Ar}}$**H**, d, 2H), 8.30 ($\mathrm{C_{Ar}}$**H**, s, 2H), 8.31 ($\mathrm{C_{Ar}}$**H**, dd, 2H), 8.64 ($\mathrm{C_{Ar}}$**H**, t, 1H) ppm. ^{13}C NMR (CDCl$_3$): 123.3 (C−**C**F$_3$, q, $^1J_{C-F}$ = 270 Hz), 126.7, 129.8, 130.1, 131.2, 131.5, 131.9, 133.1, 133.3, 133.5, 135.8, 191.3 ($\mathrm{C_{ketone}}$) ppm.

1,3,5-Tris(phenylglyoxaloyl)benzene (14a) was prepared analogous to the oxidation of diphenylacetylene described by Wolfe.[18] First, 3.0 g [7.94 mmol] of 1,3,5-tris(phenylethinyl)benzol (**13a**) are dissolved in 200 mL of anhydrous DMSO (distilled from CaH$_2$), 10.6 g [59.5 mmol] of *N*-bromosuccinimide (dried over P$_2$O$_5$) is added in one portion, and the mixture is stirred overnight at 50 °C. The oxidation is stopped by adding 200 mL of H$_2$O. The crude hexaketone is filtered off, dissolved in CHCl$_3$, and washed with NaHCO$_3$ and water. Evaporation of the solvent and two recrystallizations from 2-propanol yield 3.0 g (80%) of a yellow solid; T_m = 108 °C. IR (KBr): 1687, 1666, 1593, 1451, 1320, 1293, 1187, 1166, 1000, 948, 922, 730; 710, 643 cm^{-1}. ^{1}H NMR (CDCl$_3$): 7.54 ($\mathrm{C_{Ar}}$**H**, t, 6H), 7.72 ($\mathrm{C_{Ar}}$**H**, tt, 3H), 8.05 ($\mathrm{C_{Ar}}$**H**, dd, 6H), 8.84 ($\mathrm{C_{Ar}}$**H**, s, 3H) ppm. ^{13}C NMR (CDCl$_3$): 129.1, 130.1, 132.2, 134.5, 135.4, 135.6, 190.9 ($\mathrm{C_{ketone}}$), 192.1 ($\mathrm{C_{ketone}}$) ppm.

1,3,5-Tris[(4-*tert*-butylphenyl)glyoxaloyl]benzene (14b) and 1,3,5-Tris[4-(phenylglyoxaloyl)phenyl]benzene (14c). Reaction proceeded according to **14a**; recrystallization of the crude product **14b** from 2-propanol and hexane. Yield: 48% of a yellow solid; T_m = 197 °C. IR (KBr): 2966, 1693, 1670, 1604, 1411, 1367, 1200, 1170, 925, 851, 674 cm^{-1}. ^{1}H NMR (CDCl$_3$): 1.34 (C(C**H**$_3$)$_3$, s, 27H), 7.53 ($\mathrm{C_{Ar}}$**H**, **AA′**XX′, 6H), 7.92

(C$_{\mathbf{Ar}}$**H**, AA′**XX**′, 6H), 8.80 (C$_{Ar}$**H**, s, 3H) ppm. ^{13}C NMR (CDCl$_3$): 30.9 (C−C(**C**H$_3$)$_3$), 35.5 (C−**C**(CH$_3$)$_3$), 126.2, 129.8, 130.2, 134.7, 135.6, 159.7, 191.3 (C$_{ketone}$), 192.0 (C$_{ketone}$) ppm. **14c** recrystallization from hexane/ethyl acetate. Yield: 45% of a yellow solid; T_m = 175 °C. IR (KBr): 3055, 1676, 1599, 1450, 1394, 1322, 1212, 1175, 876, 793, 718, 688 cm^{-1}. ^{1}H NMR (CDCl$_3$): 7.51 (C$_{Ar}$**H**, t, 6H), 7.66 (C$_{Ar}$**H**, tt, 3H), 7.80 (C$_{Ar}$**H**, **AA′**XX′, 6H), 7.86 (C$_{Ar}$**H**, 3H), 7.99 (C$_{Ar}$**H**, dd, 6H), 8.09 (C$_{Ar}$**H**, AA′**XX′**, 6H) ppm. ^{13}C NMR (CDCl$_3$): 126.5, 127.8, 129.0, 129.9, 130.6, 132.2, 132.8, 134.9, 141.3, 146.5, 193.8 (C$_{ketone}$), 194.2 (C$_{ketone}$) ppm.

Poly[*m*-phenylene-3,3′-bis(2,2′-diphenyl)quinoxaline-6,6′-diyl] (10a). One gram [2.92 mmol] of 1,3-bis(phenylglyoxaloyl)benzene (**9a**) is dissolved in 10 mL of CHCl$_3$; 0.63 g [2.92 mmol] of 3,3′-diaminobenzidine is also dissolved in 10 mL of CHCl$_3$ and added in one portion. The mixture is stirred in an argon atmosphere for 1 day at room temperature and subsequently for 2 h at 60 °C. The crude polymer is purified by precipitation into MeOH and twice reprecipitated from chloroform solution. Yield: 80% of a yellow solid. IR (KBr): 1610, 1475, 1338, 1180, 1027, 830, 769, 697 cm^{-1}. ^{1}H NMR (CDCl$_3$): 7.18 (C$_{Ar}$**H**, t, 1H), 7.37 (C$_{Ar}$**H**, s(br), 4H), 7.40 (C$_{Ar}$**H**, t(br), 4H), 7.45 (C$_{Ar}$**H**, s(br), 2H), 7.55(C$_{Ar}$**H**, (br), 2H), 7.98 (C$_{Ar}$**H**, s, 1H), 8.18 (C$_{Ar}$**H**, s, 2H), 8.25 (C$_{Ar}$**H**, s, 2H), 8.54 (C$_{Ar}$**H**, s, 2H) ppm. ^{13}C NMR (CDCl$_3$): 126.2, 130.3, 132.4, 132.7, 133.0, 134.4, 134.7, 134.9, 135.9, 136.8, 138.2, 140.1, 144.6, 144.9, 146.9, 147.1, 148.2, 148.4, 153.4, 153.6, 153.8, 157.7, 158.0, 159.3 ppm.

Poly[*m*-phenylene-3,3′-bis{2,2′-di(4-*tert*-butylphenyl}quinoxaline-6,6′-diyl] (10b). Reaction proceeded according to **10a**. **10b** yield: 84% of a yellow solid. IR (KBr): 3050, 2960, 1608, 1474, 1335, 1286, 1180, 1110, 1056, 997, 886, 700 cm^{-1}. ^{1}H NMR(CDCl$_3$): 1.24 (C(C**H**$_3$)$_3$, s, 18H), 7.35 (C$_{Ar}$**H**, t, 1H), 7.41 (C$_{Ar}$**H**, **AA′**XX′, 4H), 7.52 (C$_{Ar}$**H**, dd (br), 2H), 7.55 (C$_{Ar}$**H**, AA′**XX′**,4H), 7.88 (C$_{Ar}$**H**, s, 1H), 7.90 (C$_{Ar}$**H**,s, 1H), 8.20, 8.25, 8.28 (CAr**H**$_{\mathbf{iso}}$, s (br), 2H), 8.50, 8.55 (CAr**H**, s, 2H) ppm. ^{13}C NMR (CDCl$_3$/CF$_3$CO$_2$D): 30.5 (C(CH$_3$)$_3$), 35.5 (C(CH$_3$)$_3$), 126.1, 126.4, 126.6, 127.0, 130.4, 133.1, 133.4, 133.7, 136.0, 136.2, 142.5, 143.8, 144.0, 145.0, 145.2, 150.25, 150.6, 155.0, 155.6, 155.7, 155.8 ppm.

Poly[*m*-phenylene-3,3′-bis{2,2′-di(3-trifluoromethylphenyl)}quinoxaline-6,6′-diyl (10c). Yield: 82% of a yellow solid. IR (KBr): 3060, 2900, 1612, 1580, 1477, 1325, 1167, 1126, 1051, 904, 831, 706 cm^{-1}. ^{1}H NMR (CDCl$_3$/CF$_3$CO$_2$D): 7.35 (C$_{Ar}$**H**, t, 1H), 7.48 (C$_{Ar}$**H**, s (br), 4H), 7.70 (C$_{Ar}$**H**, s (br), 4H), 8.05 (C$_{Ar}$**H**, s, 2H), 8.13 (C$_{Ar}$**H**, s, 1H), 8.25 (C$_{Ar}$**H**, s, 2H), 8.31 (C$_{Ar}$**H**, s, 2H), 8.54 (C$_{Ar}$**H**, s, 2H), 8.60 (C$_{Ar}$H, s, 2H) (all signals broad) ppm. ^{13}C NMR (CDCl$_3$/CF$_3$CO$_2$D): 125.6, 127.5, 128.2, 129.9, 130.6, 133.3, 133.7, 134.9, 135.3, 135.8, 138.6, 139.4, 144.8, 145.2, 150.6, 151.5, 151.6, 151.8, 152.6, 152.7 ppm.

The BPQs **11a−e** are prepared in an analogous manner to the synthesis of the TPQs **15a−h**.

1,3-Bis[6,7-dimethyl-3-phenylquinoxaline-2-yl]benzene (11a). Purification by column chromatography in CHCl$_3$/ethyl acetate 7:1 yields 1.0 g (90%) of a colorless glass. IR (KBr): 3050, 3023, 2922, 1725, 1549, 1480, 1335, 1203, 1064, 991, 869, 770, 697 cm^{-1}. ^{1}H NMR (CDCl$_3$): 2.5 (C−C**H**$_3$, s, 12H), 7.18 (C$_{Ar}$**H**, t, 1H), 7.35 (C$_{Ar}$**H**, dd, 4H), 7.36 (C$_{Ar}$**H**, dd, 2H), 7.48 (C$_{Ar}$**H**, dd, 2H), 7.50 (C$_{Ar}$**H**, tt, 2H), 7.85 (C$_{Ar}$**H**, t, 1H), 7.87 (C$_{Ar}$**H**, s, 2H), 7.90 (C$_{Ar}$**H**, s, 2H) ppm. ^{13}C NMR (CDCl$_3$): 20.4 (C−**C**H$_3$), 127.7, 128.1, 128.2, 128.5, 129.91, 129.94, 131.5, 139.3, 139.6, 140.1, 140.2, 140.4, 140.5, 151.9, 152.4 ppm. MS (*m*/*z* in %): 542 (100) [M$^+$]; 464 [M$^+$ − 78], 422, 377, 334 (14), 309 (23), 271 (31) [M^{2+}], 233 (15), 103 (16), 77 (12).

1,3-Bis[3-phenyl-6-trifluoromethylquinoxaline-2-yl]-benzene (11b). Purification by column chromatography in hexane/ethyl acetate 2:1 yields 85% of a colorless glass. IR (KBr): 1739, 1629, 1447, 1334, 1286, 1197, 1162, 1129, 1056, 840, 697 cm^{-1}. ^{1}H NMR (CDCl$_3$): 7.27 (C$_{Ar}$**H**, t, 1H), 7.42 (C$_{Ar}$**H**, tt, 2H), 7.55 (C$_{Ar}$**H**, t, 4H), 7.56 (C$_{Ar}$**H**, dd, 4H), 7.95 (C$_{Ar}$**H**, dd, 2H), 7.98 (C$_{Ar}$**H**, t, 1H), 8.24 (C$_{Ar}$**H**, dd, 2H), 8.51 (C$_{Ar}$**H**, s, 2H) ppm. Isomer: 7.95 (C$_{Ar}$**H**, dd, 2H), 8.29 (C$_{Ar}$**H**, dd, 2H), 8.45 (C$_{Ar}$**H**, s, 2H) ppm. ^{13}C NMR (CDCl$_3$): 123.5 (C−**C**F$_3$, q, $^1J_{C-F}$ = 270 Hz), 125.8, 127.2, 128.1, 128.4, 129.0, 129.4, 130.4, 130.6, 131.63, 131.64 (C$_{Ar}$, q, $^2J_{C-F}$ = 32 Hz), 138.3, 138.8, 140.1, 142.2, 153.9, 154.6 ppm. Isomer: 138.9, 140.1, 154.5, 155.2 ppm. MS (*m*/*z* in %): 622 (100) [M$^+$], 603, 543, 518, 450, 349 (12), 311 (9) [M^{2+}], 273, 272, 77.

1,3-Bis-[6,7-dimethyl-3-(4-*tert*-butylphenyl)quinoxaline-2-yl]benzene (11c). Purification by column chromatography in CHCl$_3$/ethyl acetate 80:1 and sublimation (10^{-5} mbar, 290 °C) yields 90% of a colorless glass. IR (KBr): 2956, 1479, 1336, 1204, 1111, 1058, 1000, 971, 870, 840, 815, 700 cm^{-1}. ^{1}H NMR (CDCl$_3$): 1.25 (C(C**H**$_3$)$_3$, s, 18H), 2.50 (C**H**$_3$, s, 12H), 7.24 (C$_{Ar}$**H**, t, 1H), 7.35 (C$_{Ar}$**H**, **AA′**XX′, 4H), 7.43 (C$_{Ar}$**H**, AA′**XX′**, 4H), 7.46 (C$_{Ar}$**H**, dd, 2H), 7.72 (C$_{Ar}$**H**, t, 1H), 7.86 (C$_{Ar}$**H**, s, 2H), 7.89 (C$_{Ar}$**H**, s, 2H) ppm. ^{13}C NMR (CDCl$_3$): 20.3 (C-**C**H$_3$), 31.1 (C(**C**H$_3$)$_3$), 34.5 (**C**(CH$_3$)$_3$), 125.1, 127.8, 128.1, 129.58, 129.61, 131.4, 136.3, 139.67, 140.0, 140.1, 140.2, 140.3, 152.0, 152.4 ppm. MS (*m*/*z* in %): 654 (100) [M$^+$], 639 (14), 597 (13), 583 (7), 541 (4), 505 (1), 464 (2), 365 (2), 365 (2), 312 (11), 291 (5), 233 (4), 57 (5).

1,3-Bis[3-(4-*tert*-butylphenyl)-6-trifluoromethylquinoxaline-2-yl]benzene (11d). Reaction proceeded according to the procedure for **11a**; purification by column chromatography in hexane/ethyl acetate 1:1 and sublimation (10^{-5} mbar, 185 °C) took place. Yield: 81% of a colorless glass. IR (KBr): 3056, 2954, 2900, 1798, 1620, 1609, 1542, 1442, 1401, 1320, 1287, 1131, 1056, 837 cm^{-1}. One isomer could be isolated to which structure **A** in Scheme 4 is assigned. ^{1}H NMR (CDCl$_3$): isomer **A** [both CF$_3$ at C6] and isomer **B** [one CF$_3$ at C6]: 1.26 (C(C**H**$_3$)$_3$, s, 18H), 7.32 (C$_{Ar}$**H15**, t, 1H), 7.40 (C$_{Ar}$**H11**, **AA′**XX′, 4H), 7.51 (C$_{Ar}$**H10**, AA′**XX′**, 4H), 7.56 (C$_{Ar}$**H14**, dd, 2H), 7.88 (C$_{Ar}$**H12**, t, 1H), 7.92 (C$_{Ar}$**H7**, dd, 2H), 8.23 (C$_{Ar}$**H8**, d, 2H), 8.48 (C$_{Ar}$**H5**, s, 2H). Isomers **B** (one CF$_3$ at C7) and **C** (both CF$_3$ at C7): 7.95 (C$_{Ar}$**H6**, dd, 2H), 8.29 (C$_{Ar}$**H5**, d, 2H), 8.45 (C$_{Ar}$**H8**, s, 2H) ppm. ^{19}F NMR (CDCl$_3$): 11.5 (CF$_3$CO$_2$H reference) ppm. ^{13}C NMR (CDCl$_3$). CF$_3$ at C6 (isomer **A** and **B**): 31.2 (C(**C**H$_3$)$_3$), 34.8 (**C**(CH$_3$)$_3$), 123.7 (C−**C**F$_3$, q, $^1J_{C-F}$ = 270 Hz), 125.4 (**C11**), 127.2 (**C7**), 127.3 (**C5**), 128.2 (**C15**), 129.7 (**C10**), 130.4 (**C14**), 130.6 (**C8**), 131.5 (**C16**), 131.7 (C$_{Ar}$, q, $^2J_{C-F}$ = 32 Hz), 135.3 (**C12**), 139.1 (**C9**,**13**), 140.3 (**C4a**), 142.1 (**C8a**), 152.8 (**C3**), 154, 7 (**C2**). Isomers with CF$_3$ at C7 (**B** and **C**): 125.55 (**C6**), 125.60 (**C8**), 130.5 (**C5**), 135.3 (**C12**), 139.0 (**C4**), 139.1 (**C9**), 140.0 (**C4a**), 142.3 (**C8a**), 154.1 (**C3**), 155.2 (**C2**) ppm. MS (*m*/*z* in %): 734 (100) [M$^+$], 719 (73), 677 (19), 663 (22), 621, 585, 449, 404, 352 (60), 329, 273, 77.

1,3-Bis[6,7-dimethyl-3-(3-trifluoromethylphenyl)quinoxaline-2-yl]benzene (11e). Purification by column chromatography in CHCl$_3$/ethyl acetate 7:1 took place. Yield: 86% of a colorless glass. IR (KBr): 3042, 2922, 1738, 1552, 1481, 1324, 1265, 1206, 1166, 1126, 1071, 1000, 870, 801 cm^{-1}. ^{1}H NMR (CDCl$_3$): 1.55 (C**H**$_3$, s, 12H), 7.21 (C$_{Ar}$**H**, t, 1H), 7.37 (C$_{Ar}$**H**, dd, 2H), 7.41 (C$_{Ar}$**H,** t, 2H), 7.56 (C$_{Ar}$**H**, d, 2H), 7.63 (C$_{Ar}$**H**, d, 2H), 7.87 (C$_{Ar}$**H**, s, 1H), 7.92 (C$_{Ar}$**H**, s, 2H), 7.97 (C$_{Ar}$**H**, t, 1H), 7.99 (C$_{Ar}$**H**, s, 2H) ppm. ^{13}C NMR (CDCl$_3$): 20.4 (C−**C**H$_3$); 124.0 (C−**C**F$_3$, q, $^1J_{C-F}$ = 270 Hz), 125.3, 126.8, 127.9, 128.1, 128.2, 128.5, 130.3, 130.9 (C$_{Ar}$, q, $^2J_{C-F}$ = 33 Hz), 131.7, 133.3, 139.1, 140.1, 140.4, 141.1, 141.2, 150.5, 151.3 ppm. MS (*m*/*z* in %): 680 (100) [M$^+$], 657, 609, 532, 463, 403, 377, 340 (13) [M^{2+}], 275, 103.

Synthetic Procedure for the Preparation of BPQs and TPQs. 1,3,5-Tris[3-phenylquinoxaline-2-yl]benzene (15a). First, 0.85 g [1.79 mmol] of 1,3,5-tris(phenylglyoxaloyl)benzene **14a** is dissolved in 150 mL of CHCl$_3$, and 0.58 g [5.37 mmol] of 4,5-dimethyl-1,2-diaminophenylenediamine **4b** is added in one portion. After 0.1 g of *p*-TSOH [0.53 mmol] is added, the mixture is refluxed for 2 days, cooled to room temperature, and washed with dilute HCl and water. Subsequent purification by column chromatography in CHCl$_3$/ethyl acetate 9:1 yields 0.95 g (77%) of a yellow solid. IR (KBr): 3056, 2923, 1725, 1478, 1444, 1337, 1201, 1086, 1005, 825, 760, 697 cm^{-1}. ^{1}H NMR (CDCl$_3$): 7.39 (C$_{Ar}$**H**, t, 3H), 7.42 (C$_{Ar}$**H**, t, 6H), 7.43 (C$_{Ar}$**H**, dd, 6H), 7.66 (C$_{Ar}$**H**, s, 3H), 7.74 (C$_{Ar}$**H**, td, 3H), 7.77 (C$_{Ar}$**H**, td, 3H), 8.04 (C$_{Ar}$**H**, **AA′**BB′, 3H), 8.15 (C$_{Ar}$**H**, AA′**BB′**, 3H) ppm. ^{13}C NMR (CDCl$_3$): 128.2, 128.9, 129.09, 129.1, 129.9, 130.1, 131.6, 138.8, 139.6, 141.1, 152.2, 153.2 ppm. MS (*m*/*z* in %): 690 (100) [M$^+$], 613, 586, 485 (16), 458, 407, 345 (14) [M^{2+}], 205 (14), 104, 77.

1,3,5-Tris[6,7-dimethyl-3-phenylquinoxaline-2-yl]benzene (15b). Purification by column chromatography in CHCl$_3$/ethyl acetate 3:1 took place. Yield: 79% of a yellow solid. IR (KBr): 3050, 3028, 2969, 2922, 1627, 1550, 1480, 1445, 1330, 1208, 1170, 1002, 868, 770 cm^{-1}. ^{1}H NMR (CDCl$_3$): 2.47 (C**H**$_3$, s, 9H), 2.49 (C**H**$_3$, s, 9H), 7.33 (C$_{\mathrm{Ar}}$**H**, tt, 3H), 7.38 (C$_{\mathrm{Ar}}$**H**, t, 6H), 7.43 (C$_{\mathrm{Ar}}$**H**, dd (br), 6H), 7.62 (C$_{\mathrm{Ar}}$**H**, s, 3H), 7.78 (C$_{\mathrm{Ar}}$**H**, s, 3H), 7.91 (C$_{\mathrm{Ar}}$**H**, s, 3H) ppm. ^{13}C NMR (CDCl$_3$): 20.3 (C−**C**H$_3$), 128.0, 128.06, 128.08, 128.6, 130.1, 131.3, 139.2, 139.8, 140.1, 140.4, 140.5, 151.5, 152.3 ppm. MS (*m*/*z* in %): 774 (100) [M$^+$], 696, 642, 541 (10), 463, 387 (13) [M^{2+}], 233.

1,3,5-Tris[3-phenyl-6-trifluoromethylquinoxaline-2-yl]-benzene (15c). Purification by column chromatography in hexane/ethyl acetate 3.5:1 and sublimation (10^{-5} mbar, 300 °C) took place. Yield: 69% of a colorless glass. IR (KBr): 3055, 1621, 1535, 1449, 1401, 1346, 1310, 1197, 1164, 1056, 1006, 902, 841 cm^{-1}. ^{1}H NMR (CDCl$_3$): 7.44−7.45 (C$_{\mathrm{Ar}}$**H**, tt, 3H), 7.45 (C$_{\mathrm{Ar}}$**H**, dd, 6H), 7.74 (C$_{\mathrm{Ar}}$**H**, s, 3H), 7.92 (C$_{\mathrm{Ar}}$**H**, dd, 6H), 8.13 (C$_{\mathrm{Ar}}$**H**, dd, 3H), 8.47 (C$_{\mathrm{Ar}}$**H**, dd, 3H). Isomers: 7.92 (C$_{\mathrm{Ar}}$**H**, dd, 3H), 8.26 (C$_{\mathrm{Ar}}$**H**, d, 3H), 8.32 (C$_{\mathrm{Ar}}$**H**, d, 3H) ppm. ^{13}C NMR (CDCl$_3$): 123.6 (C−**C**F$_3$, q, $^1J_{\mathrm{C-F}} = 270$ Hz)), 125.7, 127.3, 128.4, 129.6, 130.1, 130.4, 131.9, 132.1, 138.2, 139.2, 140.2, 142.1, 153.8, 154.5. Isomers: 140.0, 142.0, 153.2, 155.0 ppm. MS (*m*/*z* in %): 894 (100) [M$^+$], 817, 722, 621 (21), 543, 447 (13) [M^{2+}], 374, 273 (14), 209 (10), 165 (28). Anal. Calcd for $C_{51}H_{27}N_6F_9$: C, 68.46; H, 3.04; N, 9.39; F, 19.11. Found: C, 68.35; H, 3.24; N, 9.28; F, 19.12.

1,3,5-Tris[3-(4-*tert*-butylphenyl)quinoxaline-2-yl]benzene (15d). Purification column chromatography in CHCl$_3$/ethyl acetate 120:1 took place. Yield: 76% of a colorless solid. IR (KBr): 2962, 1610, 1476, 1363, 1334, 1202, 1110, 1000, 976, 846, 759 cm^{-1}. ^{1}H NMR (CDCl$_3$): 1.22 (C(C**H**$_3$)$_3$, s, 27H), 7.40 (C$_{\mathrm{Ar}}$**H**, **AA′**XX′, 6H), 7.47 (C$_{\mathrm{Ar}}$**H**, AA′**XX′**, 6H), 7.64 (C$_{\mathrm{Ar}}$**H**, s, 3H), 7.71, 8.02, 8.11 (C$_{\mathrm{Ar}}$**H**, **AA′**BB′, m, 12H) ppm. ^{13}C NMR (CDCl$_3$): 31.1 (C(**C**H$_3$)$_3$), 34.6 (**C**(CH$_3$)$_3$), 125.2, 129.2, 129.8, 130.0, 136.0, 140.2, 141.0, 141.3, 152.2, 152.6, 153.2 ppm. MS (*m*/*z* in %): 858 (100) [M$^+$], 843, 801, 745, 668, 597, 429 (1) [M^{2+}], 414, 244, 57.

1,3,5-Tris[3-(4-*tert*-butylphenyl)-6,7-dimethylquinoxaline-2-yl]benzene (15e). Purification by column chromatography in CHCl$_3$/ethyl acetate 15:1 took place. Yield: 62% of a colorless glass. IR (KBr): 2960, 1739, 1610, 1480, 1362, 1332, 1002, 969, 870, 840, 701 cm^{-1}. ^{1}H NMR (CDCl$_3$): 1.24 (C(C**H**$_3$)$_3$, s, 27H), 2.49 (C**H**$_3$, s, 9H), 2.52 (C**H**$_3$, s, 9H), 7.40 (C$_{\mathrm{Ar}}$**H**, **AA′**XX′, 6H), 7.49 (C$_{\mathrm{Ar}}$H, AA′**XX′**, 6H), 7.61 (C$_{\mathrm{Ar}}$**H**, s, 3H), 7.81 (C$_{\mathrm{Ar}}$**H**, s, 3H), 7.90 (C$_{\mathrm{Ar}}$**H**, s, 3H) ppm. ^{13}C NMR (CDCl$_3$): 20.3 (C−CH$_3$), 31.1 (C(CH$_3$)$_3$), 34.54 (C(CH$_3$)$_3$), 125.0, 128.1, 129.9, 131.1, 136.3, 139.9, 140.26, 140.5, 151.5, 151.7, 152.4 ppm. MS (*m*/*z* in %): 942 (100] [M$^+$], 886 (10), 885 (14), 855, 653, 471 (7) [M^{2+}], 273, 233, 57. Anal. Calcd for $C_{66}H_{66}N_6$: C, 84.04; H, 7.05; N, 8.91. Found: C, 83.83; H, 7.05; N, 8.86.

1,3,5-Tris[3-(4-*tert*-butylphenyl)-6-trifluoromethylquinoxaline-2-yl]benzene (15f). Purification by column chromatography in hexane/ethyl acetate 2:1 took place. Yield: 65% of a colorless glass. IR (KBr): 3070, 2954, 1919, 1741, 1610, 1543, 1399, 1322, 1057, 1003, 902, 839 cm^{-1}. ^{1}H NMR (CDCl$_3$): 1.24 (C(C**H**$_3$)$_3$, s, 27H), 7.42 (C$_{\mathrm{Ar}}$**H**, **AA′**XX′, 6H), 7.48 (C$_{\mathrm{Ar}}$**H**, AA′**XX′**, 6H), 7.70 (C$_{\mathrm{Ar}}$**H**, s, 3H), 7.88 (C$_{\mathrm{Ar}}$**H**, dd, 3H), 8.11 (C$_{\mathrm{Ar}}$**H**, d, 3H), 8.30 (C$_{\mathrm{Ar}}$**H**, s, 3H). Isomers: 7.90 (C$_{\mathrm{Ar}}$**H**, dd, 3H), 8.18 (C$_{\mathrm{Ar}}$**H**, d, 3H), 8.40 (C$_{\mathrm{Ar}}$**H**, d, 3H) ppm. ^{13}C NMR (CDCl$_3$): 31.0 (C(**C**H$_3$)$_3$), 34.7 (**C**(CH$_3$)$_3$), 123.6 (C−**C**F$_3$, q, $^1J_{\mathrm{C-F}} = 270$ Hz), 125.3, 125.6, 127.1, 130.0, 130.3, 131.6, 135.2, 139.27, 139.30, 139.6, 141.6, 153.7, 154.3. Isomers: 130.4, 131.5, 140.0, 142.0, 154.2, 154.9 ppm. MS (*m*/*z* in %): 1062 (100) [M$^+$], 1005 (11), 975, 935, 814, 733, 531 (5) [M^{2+}], 516 (17), 398, 339, 202 (1), 57 (40).

1,3,5-Tris[4-{3-phenyl-6-trifluoromethylquinoxaline-2-yl}phenyl]benzene (15g). Purification by column chromatography in hexane/ethyl acetate 2:1 took place. Yield: 65% of a light yellow-colored glass. IR (KBr): 3055, 2962, 1629, 1596, 1405, 1343, 1283, 1130, 1057, 931, 838, 696 cm^{-1}. ^{1}H NMR (CDCl$_3$): 7.42 (C$_{\mathrm{Ar}}$**H**, m, 9H), 7.61 (C$_{\mathrm{Ar}}$**H**, dd, 6H), 7.69 (C$_{\mathrm{Ar}}$**H**, s, 12H$_{\mathrm{AA'XX'}}$), 7.83 (C$_{\mathrm{Ar}}$**H**, s, 3H), 7.96 (C$_{\mathrm{Ar}}$**H**, dd, 3H), 8.31 (C$_{\mathrm{Ar}}$**H**, d, 3H), 8.51 (C$_{\mathrm{Ar}}$**H**, s, 3H) ppm. ^{13}C NMR (CDCl$_3$): 124.7 (C−**C**F$_3$, q (270 Hz)), 126.3, 126.58, 126.64, 128.2, 128.3, 129.52, 130.4, 130.5, 130.8, 130.9, 131.4, 131.5, 132.6, 138.78, 138.84, 139.49, 139.54, 141.1, 141.2, 142.5, 142.6, 143.2, 143.2, 143.2, 155.2, 155.7, 156.3 ppm. MS (*m*/*z* in %): 1122 (100) [M$^+$], 1018, 950, 875, 771, 561 (14) [M^{2+}], 349 (10), 247 (12).

1,3,5-Tris[4-{3-phenyl-6,7-dimethylquinoxaline-2-yl}-phenyl]benzene (15h). Purification by column chromatography in CHCl$_3$ took place. Yield: 63% of a yellow glass. IR (KBr): 3031, 2928, 2855, 1596, 1481, 1462, 1343, 1270, 1060, 1019, 972, 869, 838, 698 cm^{-1}. ^{1}H NMR (CDCl$_3$): 2.52 (C**H**$_3$, s, 18H), 7.56 (C$_{\mathrm{Ar}}$**H**, tt, 3H), 7.61 (C$_{\mathrm{Ar}}$**H**, s, 12H$_{\mathrm{AA'XX'}}$), 7.76 (C$_{\mathrm{Ar}}$**H**, s, 3H), 7.93 (C$_{\mathrm{Ar}}$**H**, s,6H) ppm. ^{13}C NMR (CDCl$_3$): 125.0, 126.9, 128.2, 128.3, 128.6, 129.8, 130.4, 138.6, 139.4, 140.15, 140.24, 140.5, 140.8, 141.5, 151.9, 152.4 ppm. MS (*m*/*z* in %): 1002 (100) [M$^+$], 941, 784, 694, 501 (25) [M^{2+}], 449, 347, 309, 233.

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